Some problems in the theory of molecular vibrations

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SOME PROBLEMS IN THE THEORY OF MOLECULAR VIBRATIONS.

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TO MY PARENTS

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ABSTRACT.

This thesis embodies the results of theoretical investigations into a number of branches of molecular physics in which molecular vibrations are involved. The broad divisions into which it falls are as follows: spectroscopy (Chapters I, II and III), chemical kinetics (Chapter IV), X-ray crystallography (Appendices I and II), and thermodynamics (Appendix III).

In Chapter I a new form of matrix perturbation theory is developed for calculating the vibration frequencies of molecules whose vibration spectra fall roughly into two classes, namely, a high and a low frequency class. By this method the single exact secular equation for the frequencies isreplaced by two approximate equations of lower order, in terms of whose solutions the exact frequencies are obtained as analytical but infinite series. In Chapter II it is shown that the method leads to an explicit expression for the first order effect of a bending force constant upon the skeletal stretching frequencies of normal paraffins in the zig-zag configuration. Chapter III consists of a discussion of the infra-red and Raman spectra

of helical molecules: the selection rules for fundamentals in the vibration spectra are derived from considerations of symmetry, approximate intensity relationships are found for a model containing strongly bonded atomic groupings weakly coupled together, and the perturbation theory is applied to the same model to obtain relations between the allowed fundamental frequencies and the angle of the helix.

The problem in chemical kinetics discussed in Chapter IV is that of calculating unimolecular reaction rates. An attempt is made to find a satisfactory quantum mechanical analogue of the existing classical theory.

The first two Appendices are concerned with the influence of the thermal motion of atoms in a crystal upon the electron density distributions obtained by the Fourier synthesis of X-ray diffraction data. The problem falls naturally into two parts: in I the dependence of the distribution in a carbon atom upon its thermal r.m.s. vibration amplitude is found; in II the variation of this amplitude from atom to atom within a molecular crystal is investigated.

Finally, Appendix III consists of a short note outlining a method for computing the zero-point energy of a vibrating molecule whose geometry and force field are known without first solving the secular equation for the individual frequencies.

With the exception of a few sections which summarise previous work, the material in this thesis is entirely original. Most of Chapters I and III has already been published in the form of papers (J. Chem. Phys. 21, 1131 (1953) and Proc. Roy. Soc. A220, 472 (1953), respectively). Appendices I and II contain some material which formed part of the author's M.Sc. Thesis, but there is also a considerable portion which is fresh.

NOTATION.

Throughout this thesis considerable use is made of matrix algebra. For the sake of clarity all matrices (except those in the appended printed matter) are indicated by underlining the appropriate symbol with red ink, viz. $\underline{M}$.

Everywhere except in Chapter IV a primed symbol is used to denote the transpose of a matrix: i.e. $\underline{M}'$ is the transpose of $\underline{M}$. In Chapter IV primes are already in use to distinguish the row and column parameters labelling a quantum mechanical matrix element, so to avoid confusion the transpose of $\underline{M}$ is written as $\underline{\tilde{M}}$.

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GENERAL INTRODUCTION

The theory of molecular vibrations enters into the interpretation of a wide range of phenomena in molecular physics. In the field of spectroscopy it is used to relate the observed infra-red and Raman spectra to hypothetical molecular configurations and force fields. It is employed in chemical kinetics to predict rates of reaction. It is involved in the calculation of the thermodynamic properties both of crystals and of fluids. And in electron and X-ray diffraction it comes into the interpretation of the observed spectra in terms of atomic arrangements in molecules and crystals.

In this thesis contributions are made to several of these fields. For the most part the individual chapters are self-contained, and indeed they are presented here, apart from minor modifications, in the form in which they have been published or are about to be published as papers.

Chapter I deals with a problem which is of interest mainly to spectroscopists. Given a model of a molecule in which both its equilibrium configuration and its force field are specified, it is possible in principle to solve the

secular equation for the classical vibration frequencies which appear as fundamentals in its infra-red and Raman spectra. In practice, unless the molecule is either very simple or highly symmetric, the solution entails tedious numerical computation and gives little indication of the existence of any relations between the spectra of related molecules. Nevertheless, experimentally it is found that frequencies characteristic of bonds or other small atomic groupings carry over with quite remarkable constancy from one molecule to another, as if the different modes of vibrational coupling encountered in the various molecules were of relatively slight influence. In this chapter the coupling of high frequency vibrations through low frequency structures is treated by perturbation theory and it is shown by examples under what circumstances the series so obtained for the frequencies are likely to be rapidly convergent.

In Chapter II the perturbation theory is applied to the skeletal vibrations of normal paraffins. It has long been known that a rather crude approximation to the stretching frequencies may be obtained in closed form by treating such a paraffin molecule as a perfectly flexible zigzag chain of equal point masses connected by elastic bonds. It is apparent that a better approximation is to be expected if small bending force constants are included

in the force field, but it turns out that the solution can no longer be obtained in closed form. One way of getting round this difficulty, which has been tried by earlier workers, is to treat the chain as if it were cyclic: the closed solution which results becomes valid asymptotically for long chains, but is incorrect for short chains. Another way, which is described in this chapter, is to regard the influence of the bending constants on the stretching vibrations as a small perturbation: the closed solution so derived is valid to the first order in the perturbation for all lengths of chain; it agrees asymptotically with the earlier solution for long chains as far as the first order.

The investigation reported in Chapter III is again concerned with spectroscopy. At the present time there is considerable interest in the properties of helical molecules, a class to which many substances of biological importance seem to belong. In this chapter group theory is used to classify the normal modes of such a structure and to derive the selection rules for its infra-red and Raman spectra; the relative intensities of components having various polarizations are calculated according to a weak-coupling approximation; and some approximate relations between the spectral frequencies and the number of molecular units per turn of the helix are found by an application of the

perturbation theory already described.

In Chapter IV we turn from spectra to chemical reactions. There is already in existence a theory of unimolecular reactions in which dissociation of a molecule is considered to occur when, due to vibration, a certain internal coordinate exceeds a critical value. In this theory the reaction rate is calculated by a method which treats the vibrations classically; what is done in Chapter IV is to develop a quantum mechanical analogue of the earlier theory, starting from identical assumptions with regard to the mechanism of dissociation. It is found that the quantal treatment leads to some physically absurd consequences, and it is suggested that the root of the trouble lies in the assumed definition of dissociation.

Finally, in the Appendices are collected a number of other papers, published or in course of publication. The first two of these deal with the influence of thermal vibrations in crystals upon the electron distribution derived from measurements of X-ray scattering. Preliminary investigations of this problem have already been described in Chapters 2 and 4 of the author's M.Sc. Thesis (University of London, March 1952), but the present account covers the theory more extensively than was possible at that time. Appendix III consists of a letter on a method for computing the zero-point

energy of a molecule directly from its geometry and force field.

A note on the F and G matrices.

Throughout this thesis use is made of the F and G matrix method for solving molecular vibration problems, first developed by Wilson (1939, 1941). The principal ideas of this method are summarized here for convenience.

Let the column vector $\underline{r}$ denote the 3N Cartesian components (x_1 y_1 z_1 x_2 y_2 ------ z_N) of a general displacement of an N-atomic molecule from equilibrium. The kinetic energy of the motion is the quadratic function of the velocity components

$$T = \tfrac{1}{2} \dot{\underline{r}}' \underline{M} \dot{\underline{r}}, \qquad (1)$$

in which

$$\underline{M} = \text{diag.} (m_1\ m_1\ m_1\ m_2\ m_2 \text{ ------ } m_N),$$

where m_1 ------ m_N are the masses of the N atoms. On the other hand, the potential energy depends only on the internal distortion relative to the equilibrium configuration and for small distortions may be written as a quadratic function

$$V = \tfrac{1}{2} \underline{y}' \underline{F} \underline{y}, \qquad (2)$$

in which $\underline{y}$ denotes the 3N-6 independent components (3N-5 for a linear molecule) of the internal distortion and $\underline{F}$ is a matrix of force constants and interaction constants. In

principle F may be calculated ab initio by solving the Schrödinger equation for the molecule, but in practice, such a calculation being prohibitively difficult, use is made of semi-empirical force fields based on the usual chemical model of the molecule as a structure of bonds. It is then convenient to define the components of $\underline{y}$, so far unspecified, to be extensions of bonds, deformations of bond-angles, torsions about bonds, etc., for in terms of such coordinates the F matrix may be expected to be nearly diagonal (the "simple valency force field" of Bjerrum, 1914) at least for structures of single bonds. In dealing with molecules containing double and triple bonds the same coordinates are still useful, but a more sophisticated approach to the force field is necessary, particularly where conjugated systems are involved: such an approach is provided by the molecular orbital theory of chemical binding (Coulson and Longuet-Higgins, 1948) or, qualitatively, by Pauling's resonance theory.

In general the relation between the vectors $\underline{y}$ and $\underline{r}$ in small displacements is linear and may be written in the form

$$\underline{y} = \underline{\underline{B}}\,\underline{r}\,, \qquad (3)$$

where the rectangular matrix $\underline{\underline{B}}$ may be derived from the geometry of the equilibrium configuration: general expressions

for the transformation (3) have been given by Wilson (1941) and Decius (1948). From (2) and (3) one obtains as the expression for the potential energy in terms of the Cartesian displacements

$$V = \tfrac{1}{2}\, \underline{r}'(\underline{B}'\underline{F}\,\underline{B})\,\underline{r}, \qquad (4)$$

valid only for small $\underline{r}$. The equations of motion which follow immediately from (1) and (4) may be condensed into the single matrix equation

$$\underline{M}\,\ddot{\underline{r}} = -(\underline{B}'\underline{F}\,\underline{B})\,\underline{r}. \qquad (5)$$

In order that a simple harmonic vibration, $\underline{r} \propto \cos(2\pi\nu t - \phi)$, may satisfy (5) its amplitude must fulfil the conditions

$$(\underline{B}'\underline{F}\,\underline{B})\,\underline{r} = \lambda\,\underline{M}\,\underline{r}, \qquad (6)$$

in which $\lambda = 4\pi^2\nu^2$. These equations are consistent for non-zero $\underline{r}$ only if λ is a solution of the determinantal equation

$$\left|\underline{B}'\underline{F}\,\underline{B} - \lambda\,\underline{M}\right| = 0 :$$

since the nullity of $\underline{B}'\underline{F}\,\underline{B}$ is 6, of the 3N solutions 6 are zero, corresponding to free translation and rotation.

If one is interested only in the 3N - 6 proper vibrations, one may premultiply (6) by $\underline{B}\underline{M}^{-1}$ and use (3) to obtain the more useful equations

$$\underline{G}\,\underline{F}\,\underline{y} = \lambda\,\underline{y}, \qquad (7)$$

in which

$$\underline{G} = \underline{B}\underline{M}^{-1}\underline{B}'. \qquad (8)$$

For equations (7) to be consistent either $\underline{y} = \underline{0}$ (translation and rotation) or λ is one of the 3N-6 solutions of the transformed determinantal equation

$$\left| \underline{G\,F} - \lambda\, \underline{I} \right| = 0 . \qquad (9)$$

Further analysis (see Appendix II) shows that, in fact, the kinetic energy of vibration is just the quadratic expression

$$T_{vib} = \tfrac{1}{2}\, \dot{\underline{y}}'\, \underline{G^{-1}}\, \dot{\underline{y}} , \qquad (10)$$

a relation which demonstrates the physical significance of the G matrix.

Sometimes, as in Chapter I, one is interested in the secular equations

$$\underline{x\,G\,F} = \lambda\, \underline{x}, \qquad (11)$$

where $\underline{x}$ is a row matrix, rather than in the equations (7). It is obvious from (7) and (11) that the eigenvectors $\underline{x}$ and $\underline{y}$ corresponding to a given eigenvalue λ are related by the equation

$$\left.\begin{aligned} \underline{x} &= \underline{y'\,G^{-1}} , \\ \underline{y} &= \underline{G\,x'} . \end{aligned}\right\} \qquad (12)$$

Now from (10) it follows that the momentum row matrix conjugate to the coordinate column matrix $\underline{y}$ is given by

$$\underline{p} = \dot{\underline{y}}'\, \underline{G^{-1}} .$$

Evidently, just as the eigenvector $\underline{y}$ represents (apart from an arbitrary scale factor) the amplitudes of a normal mode in coordinate space, so $\underline{x}$ represents the corresponding

amplitudes in momentum space. If $\underline{x}$ is normalized according to the convention

$$\underline{x}\, G\, \underline{x}' = 1,$$

then $\underline{y}$ is normalized to satisfy

$$\underline{y}' G^{-1} \underline{y} = 1.$$

CHAPTER I

AN APPLICATION OF PERTURBATION THEORY TO THE F AND G MATRIX METHOD OF CALCULATING MOLECULAR VIBRATION FREQUENCIES.

Summary.

The F and G matrix form of the secular equation for molecular vibrations may be split into two approximate equations, of which one has as its roots the high frequencies (corresponding to relatively rigid bonds, etc.), the other the low frequencies (corresponding to relatively weak bonds, etc.). With the aid of the eigenvectors of these two equations, the exact equation is transformed into a form which yields the corrections to the approximate frequencies by a straightforward application of perturbation theory. The use of the correction terms so derived and the convergence of the perturbation series are illustrated by a discussion of the totally symmetric modes of ethylene.

I. INTRODUCTION

The F and G matrix method described in the General Introduction is often useful in the calculation of the vibration frequencies of polyatomic molecules: its chief virtue is that it reduces the order of the secular equation

for a molecule containing N atoms from 3N to 3N-6 by eliminating the zero roots which correspond to translation and rotation. In this method the frequencies are obtained from the matrix equation

$$\underline{G F y} = \lambda \underline{y} ,$$

in which

$$\lambda = 4\pi^2 \nu^2$$

where ν is a vibration frequency, $\underline{y}$ is the column vector of internal displacements and $\underline{F}$ and $\underline{G}$ are, respectively, the potential and inverse kinetic energy matrices defined by equations G.I.(2) & (8). Then λ is a root of the determinantal equation

$$\left| \underline{G F} - \lambda \underline{I} \right| = 0 . \qquad (1)$$

Frequently it is possible and convenient to effect a further simplification by an approximate procedure. We partition the complete set of frequencies into two classes, high frequencies (A) and low frequencies (B). We may consider that these classes are related to a corresponding partition of $\underline{F}$ into large and small force constants: that is to say, writing

$$\underline{F} = \begin{pmatrix} \underline{F}_{AA} , & \underline{F}_{AB} \\ \underline{F}_{BA} , & \underline{F}_{BB} \end{pmatrix},$$

where $\underline{F}_{AA}$, $\underline{F}_{BB}$ are of orders n_A, n_B respectively

($n_A + n_B = 3N-6$) and $\underline{F}_{BA} = \underline{F}'_{AB}$, we assume that

$$\underline{F}_{AB} = \underline{0} \qquad (2)$$

(this restriction will be removed in section 5)

and that the latent roots of $\underline{F}_{AA}$ are large compared with those of $\underline{F}_{BB}$. Let the corresponding partitions of $\underline{y}$ and $\underline{G}$ be

$$\underline{y} = \begin{pmatrix} \underline{y}_A \\ \underline{y}_B \end{pmatrix} \quad \text{and} \quad \underline{G} = \begin{pmatrix} \underline{G}_{AA}, & \underline{G}_{AB} \\ \underline{G}_{BA}, & \underline{G}_{BB} \end{pmatrix},$$

where $\underline{G}_{BA} = \underline{G}'_{AB}$. The secular equation (1) becomes

$$\begin{vmatrix} \underline{G}_{AA}\underline{F}_{AA} - \lambda \underline{I}_A, & \underline{G}_{AB}\underline{F}_{BB} \\ \underline{G}_{BA}\underline{F}_{AA} , & \underline{G}_{BB}\underline{F}_{BB} - \lambda \underline{I}_B \end{vmatrix} = 0 ,$$

where $\underline{I}_A$, $\underline{I}_B$ are the unit matrices of orders n_A , n_B respectively. Obviously, if we neglect $\underline{F}_{BB}$ in comparison with $\underline{F}_{AA}$, the high frequencies are the n_A roots of the equation

$$\left| \underline{G}_{AA}\underline{F}_{AA} - \lambda_A \underline{I}_A \right| = 0 . \qquad (3a)$$

Wilson (1941) showed that when $\underline{F}_{AA}$ is large compared with $\underline{F}_{BB}$ (so that the bonds of class A are effectively rigid during normal vibrations of class B), the low frequencies are the n_B roots of the equation

$$\left| \underline{G}^*_{BB}\underline{F}_{BB} - \lambda_B \underline{I}_B \right| = 0, \qquad (3b)$$

where

$$\underline{G}^*_{BB} = \underline{G}_{BB} - \underline{G}_{BA}\underline{G}^{-1}_{AA}\underline{G}_{AB} . \qquad (4)$$

This replacement of one secular equation of order $n_A + n_B$ by two approximate ones of orders n_A and n_B often simplifies the computation considerably.

There are several instances in which the approximation is adequate: for example, the CH stretching frequency (about 3000 cm^{-1} on the wave number scale) is high compared with most of the other frequencies of organic molecules and is therefore nearly constant in all molecules, since it may be calculated from equation (3a) without reference to the structure of the rest of the molecule. Conversely, one may usually treat a CH bond as rigid in calculating the remaining frequencies from equation (3b). However, it is sometimes desirable to apply corrections to this first approximation: in this chapter the necessary correction terms are derived by an application of matrix perturbation theory. The remarkable constancy throughout a large number of molecules of the spectral frequencies associated with certain bonds or groups of bonds - the CH frequency already mentioned is a notable example - indicates that the infinite series of correction terms thus obtained may be expected to converge rapidly in many cases of importance in spectroscopy.

2. TRANSFORMATION OF THE SECULAR EQUATION

The exact secular equation which we wish to solve is

(1), in which now

$$\underline{GF} = \begin{pmatrix} \underline{G}_{AA}\,\underline{F}_{AA} , & \underline{G}_{AB}\,\underline{F}_{BB} \\ \underline{G}_{BA}\,\underline{F}_{AA} , & \underline{G}_{BB}\,\underline{F}_{BB} \end{pmatrix} .$$

Let us suppose that we have already solved the approximate equations (3a) and (3b) to obtain approximate eigenvalues which we shall denote by λ^{o}_{Ai} ($i = 1$ to n_A) and λ^{1}_{Bj} ($j = 1$ to n_B) respectively: for the present we assume these to be nondegenerate; we shall deal with the problem of degeneracy in section 4. We now calculate the corresponding row eigenvectors $\underline{x}_{Ai}$ and $\underline{x}_{Bj}$ from the matrix equations

$$\underline{x}_{Ai}\,\underline{G}_{AA}\,\underline{F}_{AA} = \lambda^{o}_{Ai}\,\underline{x}_{Ai} , \tag{5a}$$

$$\underline{x}_{Bj}\,\underline{G}^{*}_{BB}\,\underline{F}_{BB} = \lambda^{1}_{Bj}\,\underline{x}_{Bj} . \tag{5b}$$

These eigenvectors contain an arbitrary scalar factor and so may be normalized by imposing the conditions

$$\underline{x}_{Ai}\,\underline{G}_{AA}\,\underline{x}'_{Ai} = 1 , \tag{6a}$$

$$\underline{x}_{Bj}\,\underline{G}^{*}_{BB}\,\underline{x}'_{Bj} = 1 . \tag{6b}$$

By postmultiplying equation (5a) by $\underline{G}_{AA}\,\underline{x}'_{Ah}$, premultiplying the transpose of the corresponding equation in λ^{o}_{Ah} by $\underline{x}_{Ai}\,\underline{G}_{AA}$ and subtracting one from the other, we prove the eigenvectors to be orthogonal in the sense that

$$\underline{x}_{Ai}\,\underline{G}_{AA}\,\underline{x}'_{Ah} = 0 \ (i \neq h). \tag{7a}$$

Similarly we may prove that

$$\underline{x}_{Bj}\, \underline{G}^{*}_{BB}\, \underline{x}'_{Bk} = 0 \quad (j \neq k). \tag{7b}$$

Let us construct square matrices $\underline{X}_A$ and $\underline{X}_B$ from rows $\underline{x}_{Ai}$ ($i = 1$ to n_A) and $\underline{x}_{Bj}$ ($j = 1$ to n_B) respectively. Since a complete set of eigenvectors is a linearly independent set, $\underline{X}_A$ and $\underline{X}_B$ are regular. The equations (5) may now be written

$$\underline{X}_A\, \underline{G}_{AA}\, \underline{F}_{AA} = \underline{\Lambda}^{0}_{A}\, \underline{X}_A , \tag{8a}$$

$$\underline{X}_B\, \underline{G}_{BB}\, \underline{F}_{BB} = \underline{\Lambda}^{1}_{B}\, \underline{X}_B , \tag{8b}$$

where

$$\underline{\Lambda}^{0}_{A} = \operatorname{diag}(\lambda^{0}_{Ai}), \quad \underline{\Lambda}^{1}_{B} = \operatorname{diag}(\lambda^{1}_{Bj}) .$$

Equations (6) and (7) may be combined into

$$\underline{X}_A\, \underline{G}_{AA}\, \underline{X}'_A = \underline{I}_A , \tag{9a}$$

$$\underline{X}_B\, \underline{G}^{*}_{BB}\, \underline{X}'_B = \underline{I}_B . \tag{9b}$$

We next construct the matrices

$$\underline{P} = \begin{pmatrix} \underline{X}_A & , & \underline{0} \\ -\underline{X}_B\, \underline{G}_{BA}\, \underline{G}^{-1}_{AA} & , & \underline{X}_B \end{pmatrix},$$

$$\underline{Q} = \begin{pmatrix} \underline{G}_{AA}\, \underline{X}'_A & , & \underline{0} \\ \underline{G}_{BA}\, \underline{X}'_A & , & \underline{G}^{*}_{BB}\, \underline{X}'_B \end{pmatrix},$$

which are easily seen from equations (9) to be reciprocals

($\underline{PQ} = \underline{I}$). Pre- and postmultiplication of $\underline{GF}$ by $\underline{P}$ and $\underline{Q}$ respectively yields the symmetric matrix

$$\underline{H} = \underline{P\,G\,F\,Q}$$

$$= \begin{pmatrix} \underline{X}_A \underline{G}_{AA} \underline{F}_{AA} \underline{G}_{AA} \underline{X}_A' \\ + \underline{X}_A \underline{G}_{AB} \underline{F}_{BB} \underline{G}_{BA} \underline{X}_A' \end{pmatrix}, \quad \underline{X}_A \underline{G}_{AB} \underline{F}_{BB} \underline{G}^{*}_{BB} \underline{X}_B' \\ \underline{X}_B \underline{G}^{*}_{BB} \underline{F}_{BB} \underline{G}_{BA} \underline{X}_A', \quad \underline{X}_B \underline{G}^{*}_{BB} \underline{F}_{BB} \underline{G}^{*}_{BB} \underline{X}_B' \end{pmatrix}.$$

This formula may be simplified by defining the new matrices

$$\underline{\Gamma}_{AB} = \underline{X}_A \underline{G}_{AB} \underline{X}_B', \tag{10}$$

$$\underline{\Gamma}_{BA} = \underline{\Gamma}_{AB}'$$

and using equations (8) and (9):

$$\underline{H} = \begin{pmatrix} \underline{\Delta}_A^0 + \underline{\Gamma}_{AB} \underline{\Delta}_B^1 \underline{\Gamma}_{BA}, & \underline{\Gamma}_{AB} \underline{\Delta}_B^1 \\ \underline{\Delta}_B^1 \underline{\Gamma}_{BA}, & \underline{\Delta}_B^1 \end{pmatrix}. \tag{11}$$

Thus pre- and postmultiplication of the secular equation (1) by $|\underline{P}|$ and $|\underline{Q}|$ respectively transforms it to the new form

$$\left|\underline{H} - \lambda \underline{I}\right| = 0, \tag{12}$$

where $\underline{H}$ is defined by equation (11).

3. APPLICATION OF PERTURBATION THEORY

So far, in the derivation of equation (12) from the original secular equation, the theory has been exact. Now let us suppose that the frequencies of class B are low compared with those of class A, that is, that all the ratios $\lambda^1_{Bj} / \lambda^0_{Ai}$ are small. Then $\underline{\Lambda}^1_B$ may be considered as of the first order of smallness relative to $\underline{\Lambda}^0_A$, and $\underline{H}$ may be expanded as a series

$$\underline{H} = \underline{H}^0 + \underline{H}^1 ,$$

where, from (11), the zeroth and first order terms are respectively

$$\underline{H}^0 = \begin{pmatrix} \underline{\Lambda}^0_A , & \underline{O} \\ \underline{O} , & \underline{O} \end{pmatrix},$$

$$\underline{H}^1 = \begin{pmatrix} \underline{\Gamma}_{AB}\,\underline{\Lambda}^1_B\,\underline{\Gamma}_{BA} , & \underline{\Gamma}_{AB}\,\underline{\Lambda}^1_B \\ \underline{\Lambda}^1_B\,\underline{\Gamma}_{BA} , & \underline{\Lambda}^1_B \end{pmatrix}.$$

Let the corresponding infinite series for the eigenvalues be

$$\lambda_{Ai} = \lambda^0_{Ai} + \lambda^1_{Ai} + \lambda^2_{Ai} + \text{----} ,$$

$$\lambda_{Bj} = \lambda^1_{Bj} + \lambda^2_{Bj} + \lambda^3_{Bj} + \text{----} .$$

A straightforward application of perturbation theory leads

to the following expressions for the successive corrections to λ^{0}_{Ai} and λ^{1}_{Bj}.

First correction:-

$$\lambda^{1}_{Ai} = H^{1}_{Ai,Ai}$$

$$= \underline{x}_{Ai}\, \underline{G}_{AB}\, \underline{F}_{BB}\, \underline{G}_{BA}\, \underline{x}'_{Ai}$$

$$= \sum_{j=1}^{n_B} \left(\Gamma_{Ai,Bj}\right)^2 \lambda^{1}_{Bj} \,. \qquad (13)$$

$$\lambda^{2}_{Bj} = \sum_{i} H^{1}_{Bj,Ai}\, H^{1}_{Ai,Bj} \Big/ \left(\lambda^{0}_{Bj} - \lambda^{0}_{Ai}\right)$$

$$= -\underline{x}_{Bj}\, \underline{G}^{*}_{BB}\, \underline{F}_{BB}\, \underline{G}_{BA}\, \underline{G}^{-1}_{AA}\, \underline{F}^{-1}_{AA}\, \underline{G}^{-1}_{AA}\, \underline{G}_{AB}\, \underline{F}_{BB}\, \underline{G}^{*}_{BB}\, \underline{x}'_{Bj}$$

$$= -\left(\lambda^{1}_{Bj}\right)^2 \sum_{i=1}^{n_A} \left(\Gamma_{Bj,Ai}\right)^2 \Big/ \lambda^{0}_{Ai} \,. \qquad (14)$$

Second correction:-

$$\lambda^{2}_{Ai} = \sum_{h}{}' H^{1}_{Ai,Ah}\, H^{1}_{Ah,Ai} \Big/ \left(\lambda^{0}_{Ai} - \lambda^{0}_{Ah}\right)$$

$$+ \sum_{j} H^{1}_{Ai,Bj}\, H^{1}_{Bj,Ai} \Big/ \left(\lambda^{0}_{Ai} - \lambda^{0}_{Bj}\right)$$

$$= \sum_{h=1}^{n_A}{}' \left(\sum_{j=1}^{n_B} \Gamma_{Ai,Bj} \lambda^1_{Bj} \Gamma_{Bj,Ah} \right)^2 / (\lambda^0_{Ai} - \lambda^0_{Ah})$$

$$+ (\lambda^0_{Ai})^{-1} \sum_{j=1}^{n_B} \left(\Gamma_{Ai,Bj} \lambda^1_{Bj} \right)^2 .$$

$$\lambda^3_{Bj} = \sum_{i,h} H^1_{Bj,Ai} H^1_{Ai,Ah} H^1_{Ah,Bj} / (\lambda^0_{Bj} - \lambda^0_{Ai})(\lambda^0_{Bj} - \lambda^0_{Ah})$$

$$- \sum_{i} H^1_{Bj,Bj} H^1_{Bj,Ai} H^1_{Ai,Bj} / (\lambda^0_{Bj} - \lambda^0_{Ai})^2$$

$$+ \sum_{k}{}' \left\{ \sum_{i} H^1_{Bj,Ai} H^1_{Ai,Bk} / (\lambda^0_{Bj} - \lambda^0_{Ai}) \right\}^2 / (\lambda^1_{Bj} - \lambda^1_{Bk})$$

$$= (\lambda^1_{Bj})^3 \left[\sum_{k=1}^{n_B}{}' \left\{ \sum_{i=1}^{n_A} \Gamma_{Bj,Ai} (\lambda^0_{Ai})^{-1} \Gamma_{Ai,Bk} \right\}^2 \lambda^1_{Bk} / (\lambda^1_{Bj} - \lambda^1_{Bk}) \right.$$

$$\left. + \left\{ \sum_{i=1}^{n_A} (\Gamma_{Bj,Ai})^2 / \lambda^0_{Ai} \right\}^2 - \sum_{i=1}^{n_A} (\Gamma_{Bj,Ai} / \lambda^0_{Ai})^2 \right] .$$

(In the formulae for λ^2_{Ai} and λ^3_{Bj} the primed summation signs indicate that the terms h = i and k = j are to be omitted from the respective sums.)

4. REMOVAL OF DEGENERACIES

We have assumed so far that the original determinantal equations (3a) and (3b) have only distinct roots. As far as the transformation of the exact equation (1) is concerned, this is an unnecessarily restrictive assumption. The analysis which leads to equation (12) remains valid when the approximate frequencies are degenerate, provided that the degenerate row eigenvectors are chosen by a Schmidt process so as to satisfy the orthogonality conditions (7a) and (7b).

However, the application of perturbation theory to (12) yields somewhat different results in the more general case. Let us now label the distinct approximate frequencies λ^0_{Ai}, λ^1_{Bj} and use α, β to distinguish different eigenvectors of a degenerate set : thus α, β run from 1 to d_{Ai} , d_{Bj} respectively, these numbers being the degeneracies of λ^0_{Ai} , λ^1_{Bj} and therefore satisfying the relations

$$\sum_i d_{Ai} = n_A ,$$

$$\sum_j d_{Bj} = n_B .$$

Then the first correction terms are as follows:-

λ^1_{Ai} is one of the d_{Ai} roots of the equation

$$\left| H^1_{Ai\alpha\,,Ai\alpha'} - \lambda^1_{Ai}\,\delta_{\alpha\alpha'} \right| \;=\; 0\,,$$

that is,

$$\left| \underline{x}_{Ai\alpha}\,\underline{G}_{AB}\underline{F}_{BB}\underline{G}_{BA}\,\underline{x}'_{Ai\alpha'} - \lambda^1_{Ai}\,\delta_{\alpha\alpha'} \right| \;=\; 0$$

or

$$\left| \left\{ \sum_{j,\beta} \Gamma_{Ai\alpha,Bj\beta}\,\lambda^1_{Bj}\,\Gamma_{Bj\beta,Ai\alpha'} \right\} - \lambda^1_{Ai}\,\delta_{\alpha\alpha'} \right| = 0\,;$$

λ^2_{Bj} is one of the d_{Bj} roots of the equation

$$\left| \left\{ \sum_{i,\alpha} H^1_{Bj\beta,Ai\alpha}\,H^1_{Ai\alpha,Bj\beta'} \Big/ (\lambda^0_{Bj} - \lambda^0_{Ai}) \right\} - \lambda^2_{Bj}\,\delta_{\beta\beta'} \right| = 0,$$

that is,

$$\left| \left\{ -\underline{x}_{Bj\beta}\,\underline{G}^{*}_{BB}\,\underline{F}_{BB}\,\underline{G}_{BA}\,\underline{G}^{-1}_{AA}\,\underline{F}^{-1}_{AA}\,\underline{G}^{-1}_{AA}\,\underline{G}_{AB}\,\underline{F}_{BB}\,\underline{G}^{*}_{BB}\,\underline{x}'_{Bj\beta'} \right\} - \lambda^2_{Bj}\,\delta_{\beta\beta'} \right| \;=\; 0$$

or

$$\left| \left\{ -(\lambda^1_{Bj})^2 \sum_{i,\alpha} \Gamma_{Bj\beta,Ai\alpha}\,(\lambda^0_{Ai})^{-1}\,\Gamma_{Ai\alpha,Bj\beta'} \right\} - \lambda^2_{Bj}\,\delta_{\beta\beta'} \right| = 0.$$

More complicated expressions may be obtained for the second correction terms: the form of these depends upon whether the degeneracy has been entirely removed by the first correction.

5. INCLUSION OF INTERACTION CONSTANTS.

The other restrictive assumption made thus far, which is also readily removed, is the condition (2), which states that all potential constants for interaction of the coordinates of class A with those of class B are to be neglected. It is often useful to consider the effect upon the frequencies of such interaction constants and, as they are usually small, they may be treated by perturbation theory as an additional means of coupling between the A and B systems.

If $\underline{F}_{AB}$ is retained in the F matrix, the product $\underline{GF}$ has the form

$$\underline{GF} = \begin{pmatrix} \underline{G}_{AA}\,\underline{F}_{AA} + \underline{G}_{AB}\,\underline{F}_{BA} , & \underline{G}_{AA}\,\underline{F}_{AB} + \underline{G}_{AB}\,\underline{F}_{BB} \\ \underline{G}_{BA}\,\underline{F}_{AA} + \underline{G}_{BB}\,\underline{F}_{BA} , & \underline{G}_{BA}\,\underline{F}_{AB} + \underline{G}_{BB}\,\underline{F}_{BB} \end{pmatrix}.$$

After transformation by $\underline{P}$ and $\underline{Q}$ this matrix becomes

$$\underline{H} = \begin{pmatrix} \underline{\Lambda}^{\circ}_{A} + \underline{\Gamma}_{AB}\,\underline{\Phi}_{BA} + \underline{\Phi}_{AB}\,\underline{\Gamma}_{BA} + \underline{\Gamma}_{AB}\,\underline{\Lambda}^{1}_{B}\,\underline{\Gamma}_{BA} , & \underline{\Phi}_{AB} + \underline{\Gamma}_{AB}\,\underline{\Delta}^{1}_{B} \\ \underline{\Phi}_{BA} + \underline{\Lambda}^{1}_{B}\,\underline{\Gamma}_{BA} , & \underline{\Lambda}^{1}_{B} \end{pmatrix}, \tag{15}$$

in which

$$\underline{\Phi}_{AB} = \underline{X}_{A}\,\underline{G}_{AA}\,\underline{F}_{AB}\,\underline{G}^{*}_{BB}\,\underline{X}'_{B} , \tag{16}$$

$$\underline{\Phi}_{BA} = \underline{\Phi}'_{AB} .$$

The transformed secular equation is again (12), but with $\underline{H}$ now defined by (15).

In applying perturbation theory, we now treat $\underline{\Phi}_{AB}$ as a first order quantity in addition to $\underline{\Delta}^1_B$. The first order term in $\underline{H}$ is thus

$$\underline{H}^1 = \begin{pmatrix} \underline{\Gamma}_{AB}\underline{\Phi}_{BA} + \underline{\Phi}_{AB}\underline{\Gamma}_{BA} + \underline{\Gamma}_{AB}\underline{\Delta}^1_B\underline{\Gamma}_{BA}, & \underline{\Phi}_{AB} + \underline{\Gamma}_{AB}\underline{\Delta}^1_B \\ \underline{\Phi}_{BA} + \underline{\Delta}^1_B\underline{\Gamma}_{BA}, & \underline{\Delta}^1_B \end{pmatrix}.$$

So, in the case of nondegenerate approximate frequencies, the first correction terms are as follows:-

$$\lambda^1_{Ai} = \sum_{j=1}^{n_B} \Gamma_{Ai,Bj}\left(2\Phi_{Bj,Ai} + \lambda^1_{Bj}\Gamma_{Bj,Ai}\right), \qquad (17)$$

$$\lambda^2_{Bj} = -\sum_{i=1}^{n_A} \left(\Phi_{Bj,Ai} + \lambda^1_{Bj}\Gamma_{Bj,Ai}\right)^2 \Big/ \lambda^0_{Ai}. \qquad (18)$$

The corresponding second corrections may be derived from the general formulae given in section 3 in terms of $\underline{H}^1$ by substituting the appropriate expressions for the matrix elements.

It appears now that two distinct effects contribute to the frequency shifts: potential coupling, represented by the matrix $\underline{\Phi}_{AB}$; and kinetic coupling, represented by $\underline{\Gamma}_{AB}$

6. EXAMPLE : THE A_g MODES OF ETHYLENE

As a simple example of the application of the formulae derived above and to illustrate the convergence (or otherwise) of the perturbation series, let us consider the totally symmetric (A_g) modes of ethylene. There are three such modes, which may be specified roughly as follows: deformation of the HCH angles (ν_1), stretching of the CC double bond (ν_2) and stretching of the CH single bonds (ν_3). The observed wave numbers ($\tilde{\nu} = \nu/c$) listed by Herzberg (1945, p.184) are 1342, 1623 and 3019 cm^{-1} respectively.

Three of the six possible classifications of the frequencies into sets A (high) and B (low) are set out in table 1: of these, (i) is obviously the most sensible, since $\tilde{\nu}_3$ is much higher than $\tilde{\nu}_1$ and $\tilde{\nu}_2$; (ii) is more risky, for $\tilde{\nu}_1$ is not much smaller than $\tilde{\nu}_2$; (iii) reverses the order of $\tilde{\nu}_1$ and $\tilde{\nu}_2$ and may therefore be expected to yield poor approximations.

In table 2 are tabulated the approximate frequencies calculated according to each of the schemes (i), (ii) and (iii): the first entry (denoted by 0) in each section is the solution of the approximate secular equations; the other entries (labelled 1 and 2) are the same frequencies after the application of the first and second corrections

respectively. In addition, the exact solution of the cubic secular equation is given for purposes of comparison. The force constants used in the computations are those listed by Herzberg (loc. cit.), interaction constants being neglected: these are chosen to fit the whole of the ethylene spectrum (six force constants are chosen to fit a total of twelve frequencies), so the exactly calculated A_g frequencies do not agree very closely with the observed lines. This discrepancy is irrelevant to the present comparison between exact and approximate theoretical frequencies.

7. DISCUSSION

Inspection of the values of $\tilde{\nu}_1$ and $\tilde{\nu}_2$ in table 2 shows that, as was to be expected, the successive approximations of calculation (i) converge quite rapidly, those of (ii) converge rather more slowly, whereas those of (iii) appear to be divergent. One may conclude from this that when (as in (ii)) the classification into low and high frequencies is a poor one, several corrections may be necessary before reasonably accurate values are obtained for frequencies near the borderline of the classification; and that when (as in (iii)) the classification actually reverses the proper order of some of the frequencies, the crude approximate solution of the secular equations is the one which lies

closest to the exact solution for the transposed frequencies. On the other hand, the highest frequency ($\tilde{\nu}_3$) is obtained with good accuracy even by method (iii); method (ii), in which the influence of the middle frequency ($\tilde{\nu}_2$) is taken into account from the outset by including it in class A, leads to the best results. One may conclude that in the calculation of the more remote frequencies of a spectrum the method of classifying the middle frequencies is of little importance.

The amount of labour involved in applying the corrections is quite small, when once the approximate secular equations have been solved for the eigenvalues λ^0_{Ai}, λ^1_{Bj} and the corresponding eigenvectors $\underline{x}_{Ai}$, $\underline{x}_{Bj}$. The construction of the matrices $\underline{\Phi}_{AB}$ and $\underline{\Gamma}_{AB}$ and the calculation of the successive correction terms consist merely of straightforward algebraic manipulations which can be performed rapidly on a desk calculating machine. The apparent disadvantage of the procedure is that it involves finding eigenvectors as well as eigenvalues, but for large secular equations the extra labour which is entailed is small compared with that needed for the solution of the complete secular equation. For example, it is easier to compute eigenvalues and eigenvectors for two quartics than to obtain the eigenvalues of one eighth-order equation. Besides, the

solutions for certain common atomic groupings, once found, may be used over and over again in calculations on larger molecules.

Finally, one comment must be made concerning the nature of the approximation used in the derivation of the approximate secular equations. In the introduction it was stated (following the usual derivation of these equations) that the classification of the frequencies corresponds to a partition of the force constants into low and high classes, that is, to a classification of the bonds, etc. into weak and strong classes. But the transformed exact secular equation (12) shows that it is the approximate frequencies whose relative magnitudes are important; more precisely, the convergence of the perturbation series depends mainly on the ratios $\lambda^1_{Bj}/\lambda^0_{Ai}$. Thus the effective rigidity of a bond, in the sense which is important for the calculation of frequencies, depends not only on its having a relatively large force constant but also on its being attached to a relatively light atom. For example, the effective rigidity of a CH bond relative to a CC single bond is a consequence of the relatively small mass of the H atom; the force constants are not very different in magnitude.

TABLE I

METHODS OF CLASSIFYING THE ETHYLENE A_g MODES

	ν_1	ν_2	ν_3
(i)	B	B	A
(ii)	B	A	A
(iii)	A	B	A

TABLE 2

A_g FREQUENCIES OF ETHYLENE

Type of calculation.		$\tilde{\nu}_1$ (cm^{-1})	Error (%)	$\tilde{\nu}_2$ (cm^{-1})	Error (%)	$\tilde{\nu}_3$ (cm^{-1})	Error (%)
Exact		1237	-	1758	-	3013	-
	0	1238	0.1	1774	0.9	2983	- 1.0
(i)	1	1237	0.0	1763	0.3	3003	- 0.3
	2	1237	0.0	1759	0.1	3009	- 0.1
	0	1363	10.2	1598	- 9.1	3009	- 0.1
(ii)	1	1303	5.3	1664	- 5.3	3012	- 0.03
	2	1263	2.1	1710	- 2.7	3012	- 0.03
	0	1442	16.6	1522	-13.4	2985	- 0.9
(iii)	1	1534	24.0	1408	-19.9	3005	- 0.3
	2	1629	31.7	1297	-26.2	3010	- 0.1

CHAPTER II

THE SKELETAL STRETCHING VIBRATIONS OF NORMAL PARAFFINS : A PERTURBATION TREATMENT.

Summary.

The perturbation theory developed in the previous chapter is applied to the skeletal vibrations of the n-paraffins. By treating the bending force constant as small compared with the stretching constant the first order correction to the stretching frequencies is obtained in closed form. It is compared with the corresponding term in the Kirkwood - Pitzer formula for long-chain paraffins.

I. INTRODUCTION

The most stable configuration of the n-paraffins $H(CH_2)_nH$, and that which is the only form found in the crystalline state (Müller, 1928; Bunn, 1939), consists of a planar zigzag arrangement of the carbon skeleton and terminal hydrogens with the CH_2 groups disposed symmetrically in planes normal to the zigzag axis, all the angles being approximately tetrahedral. Attempts have been made to account for the frequencies of those in-plane vibrations in which the carbon skeleton suffers most of the deformation by treating the

skeleton as a zigzag chain of equal point masses. If a force field containing only a single stretching constant for each CC bond is employed, the secular equations admit of an analytic solution (Barriol, 1939), but the frequency spectrum obtained does not agree well with the infra-red and Raman data. If a bending constant for the CCC angle is now introduced, the solution is no longer analytic but approximate expressions may be derived for long chains, where end effects are comparatively unimportant, by imposing periodic boundary conditions (Kirkwood, 1939; Pitzer, 1940). By a suitable choice of the bending constant reasonable agreement with the general features of the observed spectra may be achieved (Brown, Sheppard & Simpson, 1950).

In this chapter it is shown that a treatment of the bending constant as a perturbation by the method described in Chapter I leads to a closed analytic expression for the first order correction to the stretching frequencies for all chain lengths. For long chains it is found that this expression tends asymptotically to the first order term in the Kirkwood-Pitzer formula.

In section 2 the problem is formulated in the F and G matrix formalism and the approximate secular equations I (5a) for the stretching frequencies are solved. In section 3 the first order correction term is calculated. Section 4

consists of a résumé of the Kirkwood-Pitzer solution and a comparison of that solution with the present work. The results are discussed in section 5.

2. THE SECULAR EQUATIONS.

Let us consider a regular zigzag chain of N point masses m in the xy plane, the zigzag axis lying along the x axis (see figure 1). We define internal coordinates for stretching and bending as follows:-

y_{Ar} = increment of (r, r + 1) bond length
($r = 1 \ldots\ldots N - 1$) ;

y_{Bs} = equilibrium bond length X
increment of (s, s + 1, s + 2) bond
angle ($s = 1 \ldots\ldots N - 2$).

By inspection of figure 1 we see that for small displacements the equations relating y_{Ar} , y_{Bs} to the Cartesian displacements of the masses are

$$\left.\begin{aligned} y_{Ar} &= (-x_r + x_{r+1})\sin\tfrac{1}{2}\theta + (-1)^r(y_r - y_{r+1})\cos\tfrac{1}{2}\theta \ , \\ y_{Bs} &= (-x_s + x_{s+2})\cos\tfrac{1}{2}\theta - (-1)^s(y_s - 2y_{s+1} + y_{s+2})\sin\tfrac{1}{2}\theta, \end{aligned}\right\} \quad (1)$$

where θ is the equilibrium bond angle: the coefficients of this transformation constitute the matrix $\underline{B}$ of G.I.(3). From equations (1) and G.I.(8) we find the following expressions for the non-zero elements of the G matrix:-

$$
\left.
\begin{aligned}
G_{Ar,Ar} &= 2m^{-1}, \\
G_{Ar,Ar+1} &= m^{-1}\cos\theta = G_{Ar,Ar-1}; \\
G_{Bs,Bs} &= 2m^{-1}(2-\cos\theta), \\
G_{Bs,Bs+1} &= 2m^{-1}(1-\cos\theta) = G_{Bs,Bs-1}, \\
G_{Bs,Bs+2} &= -m^{-1}\cos\theta = G_{Bs,Bs-2}; \\
G_{Ar,Bs} &= -m^{-1}\sin\theta = G_{Bs,Ar} \\
&\quad (s = r-2,\ r-1,\ r,\ r+1).
\end{aligned}
\right\} \qquad (2)
$$

These formulae are special cases of those tabulated by Decius (1948).

If we suppose that the bonds are identical and assume that the force field contains only force constants k_A, k_B for stretching and bending respectively, the F matrix takes on a particularly simple form in which the only non-zero elements are

$$
\left.
\begin{aligned}
F_{Ar,Ar} &= k_A, \\
F_{Bs,Bs} &= k_B.
\end{aligned}
\right\} \qquad (3)
$$

The secular equations G.I. (11) for the momentum vector $\underline{x}$ are now

$$
\begin{aligned}
\lambda x_{Ar} = (k_A/m)\{&(x_{Ar-1}\cos\theta + 2x_{Ar} \\
&+ x_{Ar+1}\cos\theta) - \sin\theta(x_{Br-2} + x_{Br-1} \\
&+ x_{Br} + x_{Br+1})\},
\end{aligned} \qquad (4)
$$

$$\lambda x_{Bs} = (k_B/m)\{(-x_{Bs-2}\cos\theta + 2x_{Bs-1}\overline{1-\cos\theta} + 2x_{Bs}\overline{2-\cos\theta} + 2x_{Bs+1}\overline{1-\cos\theta} - x_{Bs+2}\cos\theta) - \sin\theta\,(x_{As-1} + x_{As} + x_{As+1} + x_{As+2})\}, \qquad (4, \text{cont.d.})$$

in which $\lambda = 4\pi^2\nu^2$.

By setting $k_B = 0$ in the first of equations (4) we obtain for the approximate secular equations I (5a)

$$\lambda^o_A x_{Ar} = (k_A/m)\{2x_{Ar} + \cos\theta(x_{Ar-1} + x_{Ar+1})\}. \qquad (5)$$

The standard method of dealing with such a linear second order difference equation is to write as a trial solution

$$x_{Ar} = a \exp(i\,r\,\phi),$$

which satisfies (5) provided that

$$\lambda^o_A = (2k_A/m)(1 + \cos\theta\cos\phi). \qquad (6)$$

Obviously $\pm\phi$ give rise to the same λ^o_A, so the general solution for x_A is

$$x_{Ar} = a \exp(i\,r\,\phi) + b \exp(-i\,r\,\phi).$$

Now the boundary conditions which have to be imposed are

$$x_{A0} = 0, \quad x_{AN} = 0,$$

corresponding to the end equations $r = 1$, $N - 1$ of the set (5). Therefore the actual solution is

$$x_{Ar} = c \sin(r\phi) \qquad (7)$$

with ϕ limited to the roots of the equation

$$\sin(N\phi) = 0. \qquad (8)$$

The roots of (8) which give rise to distinct non-trivial solutions (7) are

$$\phi_j = j\pi/N, \quad j = 1 \ldots\ldots N-1. \tag{9}$$

So the approximate momentum vector in the jth normal mode has the form

$$x_{Ajr} = c_j \sin(jr\pi/N), \tag{10}$$

where c_j is so far arbitrary, and from (6) the jth approximate stretching frequency is given by

$$\lambda^{o}_{Aj} = (2k_A/m)\left\{1 + \cos\theta \cos(j\pi/N)\right\}. \tag{11}$$

3. PERTURBATION THEORY

In order to apply the perturbation theory developed in Chapter I we must normalize our solution according to the convention I (6a). On substituting from (2) and (10) this condition becomes

$$(2c_j^2/m)\left\{\sum_{r=1}^{N-1} \sin^2(jr\pi/N) + \cos\theta \sum_{r=1}^{N-2} \sin(jr\pi/N)\sin(j\overline{r+1}\,\pi/N)\right\} = 1.$$

The trigonometric series are readily summed by converting them into sums of geometric progressions: the resulting expression for the normalizing factor is

$$c_j^{-2} = (2N/m)\left\{1 + \cos\theta \cos(j\pi/N)\right\}. \tag{12}$$

We are now in a position to evaluate the first order correction to the stretching frequencies arising from the non-zero bending force constant. The formula which we require is I (13) in its second form, that is,

$$\lambda^{1}_{Aj} = \underline{x}_{Aj}\, \underline{G}_{AB}\, \underline{F}_{BB}\, \underline{G}_{BA}\, \underline{x}'_{Aj} \,. \qquad (13)$$

By substituting matrix elements from (2), (3), (10) and (12) into (13) we obtain the expression

$$\lambda^{1}_{Aj} = \frac{k_B \sin^2\theta}{Nm\{1+\cos\theta\cos(j\pi/N)\}} \sum_{s=1}^{N-2} \Big\{ \sum_{r=s-1}^{s+2} \sin(jr\pi/N) \Big\}^2 .$$

On transforming and evaluating the trigonometric sums we eventually arrive at the formula

$$\lambda^{1}_{Aj} = \frac{4k_B \sin^2\theta \cos^2(j\pi/N)\{1+\cos(j\pi/N)\}}{m\{1+\cos\theta\cos(j\pi/N)\}} \times \{1-(2/N)[1-\cos(j\pi/N)]\}. \qquad (14)$$

The exact stretching frequencies are to be derived from the equation

$$\lambda_{Aj} = \lambda^{0}_{Aj} + \lambda^{1}_{Aj} + O(k_B^2/k_A), \qquad (15)$$

where λ^0_{Aj}, λ^1_{Aj} are given by (11), (14) respectively. To evaluate the second order term we should have to solve the approximate secular equations I (5b) for the bending modes, for the second order perturbation term calculated in Chapter I cannot be transformed into a form containing explicitly only $\underline{x}_{Aj}$ and the F and G matrices. Unfortunately, the equations I (5b) are somewhat intractable when applied to this problem.

4. THE KIRKWOOD-PITZER FORMULA.

The exact secular equations (4) may be partially solved by writing as a trial solution

$$\left.\begin{aligned} x_{Ar} &= a \exp(i\, r\, \phi), \\ x_{Bs} &= b \exp(i\, s\, \phi). \end{aligned}\right\} \qquad (16)$$

By the substitution (16) we get from (4) the pair of simultaneous equations

$$\begin{aligned} \lambda a &= (k_A/m)\left\{ 2a\,(1 + \cos\theta\cos\phi) \right. \\ &\qquad \left. - 4\,b \sin\theta\, e^{-\frac{1}{2}i\phi} \cos\tfrac{1}{2}\phi \cos\phi \right\}, \\ \lambda b &= (k_B/m)\left\{ -4a \sin\theta\, e^{\frac{1}{2}i\phi} \cos\tfrac{1}{2}\phi \cos\phi \right. \\ &\qquad \left. + 4\,b\,(1 + \cos\phi)(1 - \cos\theta\cos\phi) \right\}. \end{aligned}$$

On eliminating a, b from these equations we obtain for λ the formula

$$\lambda = \alpha \pm \sqrt{(\alpha^2 - \beta^2)}, \qquad (17)$$

in which

$$\alpha = (k_A/m)\,(1 + \cos\theta\cos\phi) + (2k_B/m)\,(1 + \cos\phi)\,(1 - \cos\theta\cos\phi),$$

$$\beta^2 = (8k_Ak_B/m^2)\,(1 + \cos\phi)\sin^2\phi\ .$$

The upper branch of (17) corresponds to stretching frequencies λ_A, the lower to bending frequencies λ_B.

We run into difficulty when we try to find the allowed values of the parameter ϕ. The boundary conditions to be fulfilled are now six in number, namely

$$\left.\begin{aligned} x_{A0} = x_{AN} = x_{B-1} = x_{B0} \\ = x_{BN-1} = x_{BN} = 0. \end{aligned}\right\} \qquad (18)$$

Consequently, the general solution has to contain besides (16) not only a term corresponding to $-\phi$ but also four others, corresponding to parameters $\pm\phi'$, $\pm\phi''$ which yield the same value of λ when substituted into (17). The determinantal equation which determines the allowed values of ϕ, ϕ', ϕ'' has no simple analytic solution.

Kirkwood (1939) suggested that for long chains, where presumably end effects are comparatively unimportant, this difficulty could be avoided by replacing the true boundary conditions (18) by the requirement that the solution should be periodic, with the period equal to the chain length. That is to say, the condition to be imposed on the solution (16) is

$$x_{A0} = x_{AN}, \quad x_{B0} = x_{BN}. \tag{19}$$

The allowed values of ϕ then turn out to be

$$\phi_j = 2j\pi/N. \tag{20}$$

This solution is unsatisfactory in two respects: it yields frequencies which are degenerate in pairs, contrary to observation, and it disagrees with the exact solution (9) for $k_B = 0$.

Pitzer (1946) pointed out that it would be more reasonable to impose the condition of periodicity in <u>twice</u> the chain length, that is, to allow the ends to vibrate either in phase or in opposition (phase difference = π). The allowed values of ϕ now turn out to be just those given by (9). This is much more satisfactory: the degeneracies disappear, the solution is correct for $k_B = 0$ and there is a certain amount of agreement with the observed spectra.

Let us now expand the Pitzer formula in ascending powers of k_B/k_A. From (17) and (9) we obtain for the stretching frequencies

$$\lambda_{Aj} = \lambda^0_{Aj} + \lambda^1_{Aj} + O(k_B^2/k_A),$$

where

$$\lambda^0_{Aj} = (2k_A/m)\left\{1 + \cos\theta \cos(j\pi/N)\right\}$$

and

$$\lambda^1_{Aj} = \frac{4k_B \sin^2\theta \cos^2(j\pi/N)\{1+\cos(j\pi/N)\}}{m\{1+\cos\theta\cos(j\pi/N)\}}$$

$$(j = 1 \ldots\ldots N-1). \qquad (21)$$

The expression (21) differs from (14), the correct first order term, by the absence of the factor

$$f(N, j) = 1 - (2/N)\{1 - \cos(j\pi/N)\}. \qquad (22)$$

Evidently, as $N \to \infty$ the Pitzer formula becomes successively more accurate.

5. DISCUSSION

It is instructive, in order to estimate the relative usefulness of (14) and (17), to tabulate f(N,j) for a number of values of N and j: this is done in table 1. It appears that even for quite small values of N (e.g. N = 5) f is close to unity for j = 1; more generally, it is for small values of j that the terms (14) and (21) agree best, and this agreement improves rapidly as N increases. So the Pitzer formula (17) is likely to be reliable for calculating the lower frequencies of the stretching spectrum; for these same frequencies the correct first order term (14) is at its largest and therefore the perturbation series is likely to be insufficiently convergent. On the other hand, for

large values of j, where the correct first order term is small and the perturbation series probably converges rapidly, the Pitzer formula is likely to be inadequate.

However, there is one major obstacle in the way of a satisfactory interpretation of the paraffin skeletal frequencies on the present model. The stretching frequencies are not entirely disentangled from those of all the other modes of vibration which are symmetric with respect to the zigzag plane. In particular, the wagging frequencies of the terminal methyl groups are believed to lie very close to the upper end of the stretching spectrum (see Brown, Sheppard & Simpson, op. cit.). Thus distortion of this spectrum is likely to occur in the very region in which the perturbation formula calculated in this chapter is expected to be most reliable. Evidently some method must be found of dealing with the interaction between the skeletal stretching and methyl wagging modes before an adequate interpretation can be given of the skeletal frequencies.

TABLE I: VALUES OF f (N, j).

N	j	f(N,j)
2	1	0
3	1	0.667
	2	0
4	1	0.854
	2	0.5
	3	0.146
5	1	0.924
	2	0.724
	3	0.476
	4	0.276
6	1	0.955
	2	0.833
	3	0.667
	4	0.5
	5	0.378
8	1	0.981
	2	0.927
	3	0.846
	4	0.75
	5	0.654
	6	0.573
	7	0.519
10	1	0.990
	2	0.962
	3	0.918
	4	0.862
	5	0.8
	6	0.738
	7	0.682
	8	0.638
	9	0.610
12	1	0.994
	2	0.978
	3	0.951
	4	0.917
	5	0.876
	6	0.833
	7	0.790
	8	0.75
	9	0.715
	10	0.689
	11	0.672

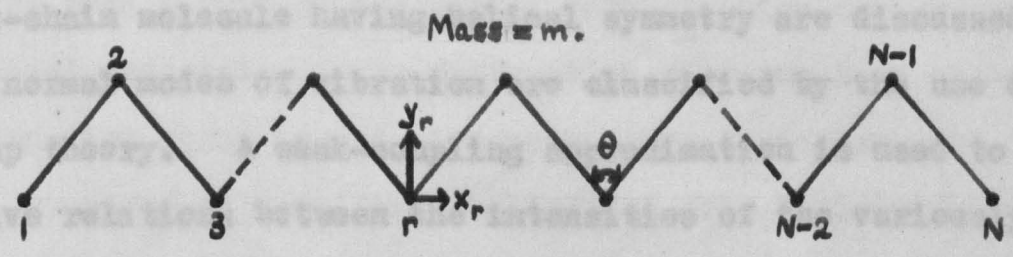

Figure 1. Model of paraffin chain.

CHAPTER III

THE VIBRATION SPECTRA OF HELICAL MOLECULES: INFRA-RED AND RAMAN SELECTION RULES, INTENSITIES AND APPROXIMATE FREQUENCIES.

Summary.

The infra-red and Raman selection rules for an infinite long-chain molecule having helical symmetry are discussed, and the normal modes of vibration are classified by the use of group theory. A weak-coupling approximation is used to derive relations between the intensities of the variously polarized spectral components arising from a single vibration frequency of the unit out of which the helix is built.

A form of matrix perturbation theory is used to obtain some approximate relations between the frequencies of these components: these relations involve the angle ψ relative to the screw axis which separates successive units of the helix and provide, in principle, a method by which this angle may be measured. It is suggested that the methods discussed here may serve as a basis for the interpretation of the spectra of fibrous proteins.

1. INTRODUCTION

Most of the current theoretical models of proteins

and synthetic polypeptides are basically helical in form: several such models have been described by Huggins (1943), by Bragg, Kendrew & Perutz (1950) and by Pauling & Corey (1951 a, b, c). The zigzag configurations proposed by Astbury & Bell (1941) and by Huggins (1943) are also of the same general type, the number of residues per turn being exactly two in these models. The experimental techniques used to investigate the structures of these molecules have so far been mainly of two sorts, both of which employ oriented material: X-ray diffraction patterns have yielded information about repeat distances along fibre axes and have been compared with patterns calculated from various theoretical models; infra-red dichroisms have led to values of the bond-axis angle for individual bonds (usually C = O and N-H) in a fibre. As has been pointed out recently by Fraser & Price (1952), whereas the interpretation of X-ray data proceeds according to a well-established general theory, the interpretation of infra-red dichroisms depends on prior knowledge of the directions of the transition moments associated with the various normal modes of vibration of the peptide residue, a fact which introduces considerable uncertainty into such interpretations.

Apart from the identification of characteristic absorption bands and the measurement of dichroic ratios, very

little use seems to have been made of the infra-red spectra so far obtained; the corresponding Raman spectra do not appear to have been investigated at all. This situation is presumably in part the result of the lack of a suitable theoretical treatment: in the case of comparatively simple molecules, for which the theory is relatively straightforward, the analysis of infra-red and Raman spectra has long been a major tool in structure investigation. It seems worthwhile therefore to consider in a fairly general manner the normal modes of vibration of a helical molecule. In this chapter group theory is used to classify the modes and to derive the selection rules for infra-red and Raman spectra; the relative intensities of components having various polarizations are calculated according to a weak-coupling approximation; and some approximate relations between the spectral frequencies and the number of residues per turn of the helix are found by an application of perturbation theory.

2. GROUP THEORY AND SELECTION RULES

Let us consider an infinite helical molecule, built up by linking together identical units (e.g. peptide residues) in such a way that each unit is transformed geometrically into the next by the operation $H(l, \psi)$ = translation through a distance l along an axis plus rotation through an angle ψ

about the same axis (figure 1.). The set of all operations H^n (n = any integer, positive or negative) which transform one unit into another constitutes an infinite group, $\underline{H}(l, \psi)$, which is simply isomorphic with the infinite cyclic group $\underline{C}_\infty$. Its irreducible representations are therefore all one-dimensional and may be labelled $\Gamma(\theta)$ with a parameter θ which runs through all values in the range, $-\pi < \theta \leq +\pi$: the corresponding characters are

$$\chi(\theta, H^n) = e^{in\theta} . \qquad (1)$$

Every normal mode of vibration of the helix must belong to one of these representations, that is, if in a normal mode a certain unit vibrates in some manner with an amplitude A, then the nth unit farther on must vibrate in the same manner with an amplitude $Ae^{-in\theta}$. Each frequency ν_i of an isolated unit gives rise in the helically linked molecule to a band of frequencies $\nu_i(\theta)$, where θ is the phase difference between the motions of adjacent units. It is easily shown that to each frequency $\nu_i(\theta)$ there corresponds a frequency $\nu_i(-\theta)$, which is the complex conjugate of $\nu_i(\theta)$ and is therefore equal to it, the frequencies being real quantities. Thus, with the exception of $\nu_i(0)$ and $\nu_i(\pi)$, the frequencies are degenerate in pairs belonging to $\Gamma(\theta)$ and $\Gamma(-\theta)$ $(0 < \theta < \pi)$: the corresponding complex normal modes may therefore be combined to form two real ones in

which the amplitudes vary as A cos nθ and A sin nθ.

Infra-red selection rules

The only frequencies which appear as allowed fundamentals in infra-red absorption are those belonging to representations $\Gamma(\theta)$ which are contained in the representation $\Gamma(\underline{M})$ which has as its basis the components of the total molecular electric dipole moment $\underline{M}$ (Rosenthal & Murphy 1936). Since $\underline{M}$ is a vector it transforms like $\underline{x}$, a typical displacement vector with components (x, y, z) relative to the axes of figure 1:

$$H^n\underline{x} = \begin{pmatrix} \cos n\psi, & -\sin n\psi, & 0 \\ \sin n\psi, & \cos n\psi, & 0 \\ 0, & 0, & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}. \qquad (2)$$

It is convenient to introduce complex coordinates

$$\left.\begin{aligned} x_+ &= (x+iy)/\sqrt{2}, \\ x_- &= (x-iy)/\sqrt{2}, \\ x_0 &= z \qquad\qquad : \end{aligned}\right\} \qquad (3)$$

the corresponding components of electric moment (M_+, M_-, M_0) are involved in the absorption of radiation with right or left-handed circular polarization about the screw-axis, or linear polarization along the screw-axis, respectively. The

transformation of $\underline{x}$ by H^n now becomes

$$\left.\begin{aligned} H^n x_+ &= e^{in\psi}\, x_+ , \\ H^n x_- &= e^{-in\psi}\, x_- , \\ H^n x_0 &= \qquad x_0 . \end{aligned}\right\} \qquad (2a)$$

Comparison of (1) and (2a) shows that x_+, x_-, x_0 belong to the irreducible representations $\Gamma(+\psi), \Gamma(-\psi), \Gamma(0)$ respectively. The infra-red selection rules are therefore those set out in table 1 (a). Since each frequency $\nu_i(\psi)$ is degenerate, it occurs in both circularly polarized components of the spectrum: transformation of the coordinates back to the system (x, y, z) shows that $\nu_i(\psi)$ is absorbed in both perpendicularly polarized (x or y) components, so an alternative set of selection rules is that of table 1 (b).

Raman selection rules

The only frequencies which are allowed as fundamentals in Raman scattering are those belonging to representations $\Gamma(\theta)$ which are contained in the representation $\Gamma(\underline{\alpha})$ which has as its basis the components of the total molecular electric polarizability $\underline{\alpha}$ (Rosenthal & Murphy 1936). Now $\underline{\alpha}$, defined by the equation

$$\underline{p} = \underline{\alpha}\,\underline{E} , \qquad (4)$$

where $\underline{E}$ is the incident radiation field and $\underline{p}$ is the induced

electric moment, is a mixed second-order tensor: its components are symmetric ($\alpha^y_x = \alpha^x_y$, etc.) when referred to Cartesian coordinates; relative to the complex coordinates defined by (3), its components form a Hermitean matrix

$$\begin{pmatrix} \alpha^+_+ , \alpha^+_- , \alpha^+_o \\ \alpha^-_+ , \alpha^-_- , \alpha^-_o \\ \alpha^o_+ , \alpha^o_- , \alpha^o_o \end{pmatrix} = \begin{pmatrix} a_o , a_2 , a_1 \\ \bar{a}_2 , a_o , \bar{a}_1 \\ \bar{a}_1 , a_1 , a'_o \end{pmatrix}. \qquad (5)$$

where

$$\left.\begin{aligned} a_o &= (\alpha^x_x + \alpha^y_y)/2 , \\ a'_o &= \alpha^z_z , \\ a_1 &= (\alpha^x_z + i\alpha^y_z)/\sqrt{2} \\ a_2 &= (\alpha^x_x - \alpha^y_y + 2i\alpha^x_y)/2. \end{aligned}\right\} \qquad (6)$$

It therefore transforms like $\underline{\underline{xx}}$: from equation (2a) we obtain the transformations

$$\left.\begin{aligned} H^n\alpha^+_+ &= \alpha^+_+, \quad H^n\alpha^+_- = e^{2in\psi}\alpha^+_-, \quad H^n\alpha^+_o = e^{in\psi}\alpha^+_o, \\ H^n\alpha^-_+ &= e^{-2in\psi}\alpha^-_+, \quad H^n\alpha^-_- = \alpha^-_-, \quad H^n\alpha^-_o = e^{-in\psi}\alpha^-_o, \\ H^n\alpha^o_+ &= e^{-in\psi}\alpha^o_+, \quad H^n\alpha^o_- = e^{in\psi}\alpha^o_-, \quad H^n\alpha^o_o = \alpha^o_o. \end{aligned}\right\} \qquad (7)$$

Comparison of (1) and (7) shows that α_+^+, α_-^- and α_0^0 belong to $\Gamma(0)$, α_0^+ and α_-^0 to $\Gamma(\psi)$, α_0^- and α_+^0 to $\Gamma(-\psi)$, α_-^+ to $\Gamma(2\psi)$ and α_+^- to $\Gamma(-2\psi)$. The Raman selection rules (in terms of two kinds of circular polarization and one of linear polarization) are therefore those set out in table 2a); transformation back to Cartesian components yields the alternative rules (in terms of three directions of linear polarization) given in table 2 (b).

It appears that the Raman spectrum contains a third set of frequencies, $\nu_i(2\psi)$, in addition to the two, $\nu_i(0)$ and $\nu_i(\psi)$, which are allowed in the parallel and perpendicular infra-red spectra respectively. This set is allowed only when both the incident and scattered beams have the electric vector vibrating perpendicular to the axis.

3. INTENSITIES

Let us suppose that in the normal modes corresponding to a certain band of frequencies, $\nu_i(\theta)$, the coupling between the motions of the units is weak, so that the width of the band is small. (This assumption seems to be valid for modes such as the characteristic NH and CO vibrations of polypeptide chains - the parallel ($\theta = 0$) and perpendicular ($\theta = \psi$) infra-red bands observed by Ambrose & Elliott (1951a,b), Fraser (1952) and others exhibit only small differences in the

positions of the absorption maxima.) Then the atomic motions of a particular unit in any one of the modes in the band are approximately the same as those in the mode ν_i of the isolated unit from which the band is generated: the various modes in the band differ one from another only in the relative phase θ of the motions of neighbouring units. In these circumstances the electric moment variation, $\underline{M}_i$, and polarizability variation, $\underline{\alpha}_i$, of the unit in the mode $\nu_i(\theta)$ are independent of θ.

Infra-red intensities

The intensity of infra-red absorption at the frequency $\nu_i(\theta)$ is (see Herzberg, 1945, chapter 3)

$$I_p[\nu_i(\theta)] = f[\nu_i(\theta)] \left| \sum_{n=-\infty}^{+\infty} M_p[n, \nu_i(\theta)] \Big/ \sum_{n=-\infty}^{+\infty} 1 \right|^2, \qquad (8)$$

in which the suffix p denotes the polarization, f is a frequency-dependent factor and $M_p[n, \nu_i(\theta)]$ is the pth component of the moment of the nth unit in the mode $\nu_i(\theta)$. According to the weak-coupling approximation, the moments corresponding to various values of θ in a particular band i differ only in the phase lags between the moment of one unit and those equivalent moments into which it is transformed by the operations of $\underline{H}$. That is,

$$M_p[n, \nu_i(\theta)] = M_{pi}(n)\, e^{-in\theta},$$

in which $M_{pi}(n)$ is that component of the moment of the nth unit into which M_{pi}, the pth component of the moment of the zeroth unit, is transformed by the operation H^n. Now the complex components are transformed according to the scheme,

$$M_{+i}(n) = M_{+i}\, e^{in\psi},$$
$$M_{-i}(n) = M_{-i}\, e^{-in\psi},$$
$$M_{oi}(n) = M_{oi},$$

so equation (8) becomes

$$I_+[\nu_i(\theta)] = f[\nu_i(\theta)] \left| \text{Av. } M_{+i}\, e^{-in(\theta-\psi)} \right|^2,$$
$$I_-[\nu_i(\theta)] = f[\nu_i(\theta)] \left| \text{Av. } M_{-i}\, e^{-in(\theta+\psi)} \right|^2,$$
$$I_o[\nu_i(\theta)] = f[\nu_i(\theta)] \left| \text{Av. } M_{oi}\, e^{-in\theta} \right|^2.$$

The only non-zero intensities are those allowed by the selection rules:-

$$\left.\begin{aligned} I_+[\nu_i(\psi)] &= f[\nu_i(\psi)] \left| M_{+i} \right|^2, \\ I_-[\nu_i(-\psi)] &= f[\nu_i(-\psi)] \left| M_{-i} \right|^2, \\ I_o[\nu_i(0)] &= f[\nu_i(0)] \left| M_{oi} \right|^2. \end{aligned}\right\} \qquad (9)$$

According to the assumption which has been made that the band $\nu_i(\theta)$ is narrow, the variation within the band of the frequency factor f may be neglected: then, from (9), the intensities of the two circularly polarized and one linearly

polarized components may be written

$$\left.\begin{aligned} I_{+i} &= f_i \left|M_{+i}\right|^2, \\ I_{-i} &= f_i \left|M_{-i}\right|^2 \quad (= I_{+i}), \\ I_{oi} &= f_i \left|M_{oi}\right|^2. \end{aligned}\right\} \tag{9a}$$

Alternatively, in terms of linearly polarized components we obtain the formulae

$$\left.\begin{aligned} I_{xi} = I_{yi} &= \tfrac{1}{2} f_i \left(M_{xi}^2 + M_{yi}^2\right), \\ I_{zi} &= f_i M_{zi}^2 . \end{aligned}\right\} \tag{9b}$$

If the transition moment $\underline{M}_i$ makes an angle ϕ_i with the axis, then

$$\left|M_{+i}\right| = (M_i/\sqrt{2}) \sin\phi_i$$

and

$$M_{oi} = M_i \cos\phi_i .$$

The resulting formulae for the intensities are tabulated in the last column of table 1. An immediate consequence is the familiar expression for the dichroic ratio

$$I_{xi}/I_{zi} = \tfrac{1}{2} \tan^2\phi_i . \tag{10}$$

Raman intensities

The intensity of vibrational Raman scattering per unit intensity of the incident radiation at a frequency-displacement $\nu_i(\theta)$ from the exciting line is (see Herzberg, loc. cit.)

$$I_p^q[\nu_i(\theta)] = g[\nu_i(\theta)]\left|\sum_{n=-\infty}^{+\infty}\alpha_p^q[n,\nu_i(\theta)]\Big/\sum_{n=-\infty}^{+\infty}1\right|^2, \quad (11)$$

in which p and q denote the polarizations of the incident and scattered beams respectively, g is a frequency-dependent factor and $\alpha_p^q[n,\nu_i(\theta)]$ is the pq-component of the polarizability variation of the nth unit in the mode $\nu_i(\theta)$. The calculation is closely similar to that of the previous section; it leads to the following expressions for the intensities of the allowed Raman lines:

$$\left.\begin{aligned}
I_+^+[\nu_i(0)] &= g[\nu_i(0)]\ |\alpha_{+i}^+|^2,\\
I_-^+[\nu_i(2\psi)] &= g[\nu_i(2\psi)]\ |\alpha_{-i}^+|^2,\\
I_o^+[\nu_i(\psi)] &= g[\nu_i(\psi)]\ |\alpha_{oi}^+|^2,\\
I_+^-[\nu_i(-2\psi)] &= g[\nu_i(-2\psi)]\ |\alpha_{+i}^-|^2,\\
I_-^-[\nu_i(0)] &= g[\nu_i(0)]\ |\alpha_{-i}^-|^2,\\
I_o^-[\nu_i(-\psi)] &= g[\nu_i(-\psi)]\ |\alpha_{oi}^-|^2,\\
I_+^o[\nu_i(-\psi)] &= g[\nu_i(-\psi)]\ |\alpha_{+i}^o|^2,\\
I_-^o[\nu_i(\psi)] &= g[\nu_i(\psi)]\ |\alpha_{-i}^o|^2,\\
I_o^o[\nu_i(0)] &= g[\nu_i(0)]\ |\alpha_{oi}^o|^2.
\end{aligned}\right\} \quad (12)$$

Neglecting variations of g within a band $\nu_i(\theta)$ and using equation (5), we find from (12) that the Raman intensities in terms of the two circular and one linear polarizations of the incident and scattered beams are

$$\left.\begin{aligned} I^{+}_{+i} &= I^{-}_{-i} = g_i (a_{oi})^2, \\ I^{o}_{oi} &= g_i (a'_{oi})^2, \\ I^{+}_{oi} &= I^{-}_{oi} = I^{o}_{+i} = I^{o}_{-i} = g_i |a_{1i}|^2, \\ I^{+}_{-i} &= I^{-}_{+i} = g_i |a_{2i}|^2, \end{aligned}\right\} \qquad (12a)$$

where a_{oi}, a'_{oi}, a_{1i}, a_{2i} are the quantities defined by equation (6), now referred to the mode ν_i of a single unit. Alternatively, the intensities in terms of three linear polarizations are

$$\left.\begin{aligned} I^{x}_{xi} = I^{y}_{yi} &= \begin{cases} g_i (a_{oi})^2 & \text{at } \nu_i(0), \\ \tfrac{1}{2} g_i |a_{2i}|^2 & \text{at } \nu_i(2\psi), \end{cases} \\ I^{x}_{yi} = I^{y}_{xi} &= \tfrac{1}{2} g_i |a_{2i}|^2 \quad \text{at } \nu_i(2\psi), \\ I^{x}_{zi} = I^{y}_{zi} &= I^{z}_{xi} \\ &= I^{z}_{yi} = g_i |a_{1i}|^2 \quad \text{at } \nu_i(\psi), \\ I^{z}_{zi} &= g_i (a'_{oi})^2 \quad \text{at } \nu_i(0). \end{aligned}\right\} \qquad (12b)$$

These formulae are tabulated in the last column of table 2.

The quantities a_{oi}, etc. which occur in the expressions

for the intensities may be related to the principal polarizabilities, α_{ri} (r = 1, 2, 3), of the unit in the mode ν_i and to the orientation of the polarizability tensor $\underline{\alpha}_i$ relative to the axis of the helix. Let ϕ_{ri} be the angle between the screw-axis and the rth principal axis of the tensor: only two of the three angles are independent, on account of the relation

$$\sum_{r=1}^{3} \cos^2 \phi_{ri} = 1. \qquad (13)$$

Some straightforward manipulation of the equations (6), when the Cartesian components of $\underline{\alpha}_i$ are expressed in terms of α_{ri} and ϕ_{ri} (r = 1, 2, 3), leads to the formulae

$$\left.\begin{aligned}
a_{oi} &= \tfrac{1}{2} \sum_{r=1}^{3} \alpha_{ri} \sin^2 \phi_{ri}, \\
a'_{oi} &= \sum_{r=1}^{3} \alpha_{ri} \cos^2 \phi_{ri}, \\
|a_{1i}|^2 &= \tfrac{1}{2} \left\{ \sum_{r=1}^{3} \alpha_{ri}^2 \cos^2 \phi_{ri} - \left(\sum_{r=1}^{3} \alpha_{ri} \cos^2 \phi_{ri} \right)^2 \right\}, \\
|a_{2i}|^2 &= \tfrac{1}{2} \left\{ \sum_{r=1}^{3} \alpha_{ri}^2 (\sin^2 \phi_{ri} - \cos^2 \phi_{ri}) \right. \\
&\qquad \left. + \left(\sum_{r=1}^{3} \alpha_{ri} \cos^2 \phi_{ri} \right)^2 - \tfrac{1}{2} \left(\sum_{r=1}^{3} \alpha_{ri} \sin^2 \phi_{ri} \right)^2 \right\}.
\end{aligned}\right\} \qquad (14)$$

Unfortunately, whereas the two independent infra-red intensities suffice to determine the two parameters, M_i and ϕ_i, the four independent Raman intensities are not sufficient to determine the five independent parameters, α_{ri} (r = 1, 2, 3) and ϕ_{ri} (r = 1, 2).

However, there is a case of possible interest in which the Raman data do fix the values of all the parameters (apart from an ambiguity of sign which is of no importance). This occurs when two of the principal polarizability variations are equal ($\alpha_2 = \alpha_3 = \alpha$, $\alpha_1 = \alpha'$, say): such a situation might occur in a vibration consisting mainly of the stretching of a single bond - one would expect the polarizability variation to be roughly symmetrical about the bond as an axis of revolution. If the x-axis is chosen so that in the selected unit the axis of revolution lies in the xz-plane, then the equations (6) assume the simple form

$$\left.\begin{aligned} a_{0i} &= \tfrac{1}{2}\{\alpha_i(1+\cos^2\phi_i)+\alpha_i' \sin^2\phi_i\}, \\ a'_{0i} &= \alpha_i \sin^2\phi_i + \alpha_i' \cos^2\phi_i, \\ a_{1i} &= -1/\sqrt{2}\,(\alpha_i - \alpha_i')\sin\phi_i \cos\phi_i, \\ a_{2i} &= -\tfrac{1}{2}\,(\alpha_i - \alpha_i')\sin^2\phi_i, \end{aligned}\right\} \qquad (15)$$

in which ϕ_i is the angle between the axis of the helix and that of the polarizability tensor. Obviously ϕ_i may now be determined from the intensity ratio

$$I^y_{xi} / I^z_{xi} = \tfrac{1}{2} \left| a_{2i} / a_{1i} \right|^2 = \tfrac{1}{4} \tan^2 \phi_i , \qquad (16)$$

a quantity analogous to the infra-red dichroic ratio. The principal polarizability variations perpendicular (α_i) and parallel (α'_i) to the band may also be determined from the intensities by using equations (12) and (15). In fact we now have three parameters (α_i , α'_i , ϕ_i) determining four Raman components (related to a_{0i}, a'_{0i}, a_{1i}, a_{2i}), so there must be some relation connecting the intensities. This relation, which follows immediately from (15), is

$$a_{2i} (a'_{0i} - a_{0i}) = a^2_{1i} - a^2_{2i}$$

or, in terms of the intensities,

$$\sqrt{I^+_{-i}} \left(\pm \sqrt{I^0_{0i}} \pm \sqrt{I^+_{+i}} \right) = I^+_{0i} - I^+_{-i} \qquad (17)$$

- or the equivalent relation involving linearly polarized

components. (The ambiguities of sign here arise from the ambiguity of sign of the amplitude a corresponding to any given positive intensity I : the signs of the polarizability components a_{oi}, a'_{oi}, a_{2i} determine which is the appropriate form of equation (17) in any particular situation.) Unless this condition is satisfied experimentally, the theoretical analysis in terms of an axially symmetric polarizability variation is not valid.

4. SECULAR EQUATIONS FOR THE FREQUENCIES

Let us label the internal coordinates $\underline{y}$ (bond extensions, angular deformations, etc.) which specify a general displacement of the molecule from equilibrium with two suffixes, r (= any positive or negative integer) numbering the units, and α (= 1, 2 .... N, where N is the number of coordinates per unit) numbering the different coordinates within a particular unit. The coordinates are to be chosen in the same manner with respect to each unit, so that members of the set $y_{r\alpha}$ (various r, fixed α) transform into one another under the operations of the group $\underline{H}$. The secular equation for internal vibrations may be set up by the method described in the General Introduction in terms of the matrices $\underline{F}$ and $\underline{G}$, such that the potential and kinetic energies of internal motion are respectively

$$V = \tfrac{1}{2}\, \underline{y}'\, \underline{F}\, \underline{y}$$

and $$T = \tfrac{1}{2}\, \dot{\underline{y}}'\, \underline{G}^{-1}\, \dot{\underline{y}}$$

in matrix notation. Then the equation to be solved for the frequencies $\nu_i(\theta)$ is

$$|\underline{GF} - \lambda \underline{I}| = 0, \tag{18}$$

in which $\lambda = 4\pi^2\nu^2$ and $\underline{I}$ is the unit matrix.

Since V and T are invariant under the operations of $\underline{H}$, it follows that the matrix elements, $F_{r\alpha,s\beta}$ and $G_{r\alpha,s\beta}$, depend on r and s only through their difference: i.e. we may write

$$F_{r\alpha,s\beta} = F^{(m)}_{\alpha\beta},$$

$$G_{r\alpha,s\beta} = G^{(m)}_{\alpha\beta},$$

where $m = s - r$. Thus $F^{(m)}_{\alpha\beta}$ represents the interaction between the αth coordinate in one unit and the βth coordinate in the mth unit farther on, and $G^{(m)}_{\alpha\beta}$ represents the corresponding kinetic coupling. By a transformation to symmetry coordinates

$$\left.\begin{aligned} s_\alpha(\theta) &= (2\pi)^{-\frac{1}{2}} \sum_{r=-\infty}^{+\infty} y_{r\alpha}\, e^{ir\theta}, \\ y_{r\alpha} &= (2\pi)^{-\frac{1}{2}} \int_{-\pi}^{+\pi} s_\alpha(\theta)\, e^{-ir\theta}\, d\theta \end{aligned}\right\} \tag{19}$$

the matrices $\underline{F}$ and $\underline{G}$ may be partially diagonalized. The result of the transformation is to put V and T into the form

$$V = \tfrac{1}{2} \int_{-\pi}^{+\pi} \underline{\bar{s}}(\theta)\, \underline{F}(\theta)\, \underline{s}(\theta)\, d\theta,$$

$$T = \tfrac{1}{2} \int_{-\pi}^{+\pi} \underline{\dot{\bar{s}}}(\theta)\, \underline{G}^{-1}(\theta)\, \underline{\dot{s}}(\theta)\, d\theta,$$

where $\underline{\bar{s}}$ is the Hermitean conjugate of $\underline{s}$ and

$$\left.\begin{aligned} F_{\alpha\beta}(\theta) &= \sum_{m=-\infty}^{+\infty} F_{\alpha\beta}^{(m)}\, e^{-im\theta}, \\ G_{\alpha\beta}(\theta) &= \sum_{m=-\infty}^{+\infty} G_{\alpha\beta}^{(m)}\, e^{-im\theta}. \end{aligned}\right\} \qquad (20)$$

Thus the transformation (19) reduces the secular equation (18), which is of infinite order, to the set of Nth order equations

$$\left| \underline{G}(\theta)\, \underline{F}(\theta) - \lambda(\theta)\, \underline{I} \right| = 0, \qquad (21)$$

in which $\underline{F}(\theta)$, $\underline{G}(\theta)$ are defined by (20),

$$\lambda(\theta) = 4\pi^2 \nu^2(\theta) \quad \text{and} \quad -\pi < \theta \leq +\pi.$$

To calculate the infra-red and Raman fundamentals for a helical molecule of given geometry and force-constants, only three equations of the set (21) need to be solved, namely those

corresponding to $\theta = 0, \psi, 2\psi$.

5. A MODEL CONTAINING MULTIPLE WEAK LINKAGES

Let us consider a helix which is built up from strongly bonded groups of atoms (to be described by internal coordinates of set A), multiply linked by weak bonds (described by coordinates of set B) - the model is shown schematically in figure 2. Making certain assumptions concerning the nature of the linkages, we shall set up the secular equations in terms of the complete set of internal coordinates (A + B) describing the unit of the helix, and by an application of perturbation theory shall derive some approximate relations between the spectral frequencies.

The assumptions to be made about the form of the F-matrix are as follows: there are no interactions between A-coordinates and B-coordinates, or between A-coordinates in different units, or between B-coordinates in different units, i.e.

$$\left.\begin{aligned} \underline{F}^{(m)}_{AB} = \underline{0}\,, \quad \underline{F}^{(m)}_{BA} = \underline{0} \ (\text{all } m), \\ \underline{F}^{(m)}_{AA} = \underline{0}\,, \quad \underline{F}^{(m)}_{BB} = \underline{0} \ (m \neq 0). \end{aligned}\right\} \qquad (22)$$

This is essentially an approximation to the force field, which may be a reasonable one if the coordinates are suitably chosen.

From (20) and (22) we obtain the F-matrix in the partitioned form

$$\underline{F}(\theta) = \begin{pmatrix} \underline{F}^{(0)}_{AA} , & \underline{O} \\ \underline{O} , & \underline{F}^{(0)}_{BB} \end{pmatrix}. \qquad (23)$$

In dealing with the G-matrix we are not entirely free to assume that certain elements vanish: except in certain special circumstances the vanishing of an element implies that the two coordinates involved have no atom in common (Wilson 1939, 1941). Any assumptions that we make must therefore be in the nature of a choice of coordinates: the choice is to be such as to simplify the G-matrix, and it is to be assumed that the potential is then adequately described in terms of these coordinates by an F-matrix of the approximate form (22). The assumption that we make here may be stated in general terms, that the kinetic coupling between the units is of the nearest-neighbour type. In detail, the assumptions are (i) that the B-coordinates provide the sole connection between the otherwise isolated A-units, (ii) that the B-coordinates link only nearest-neighbouring A-units, and (iii) that only B-coordinates in the same or in nearest-neighbouring B-links may have an atom in common. The

resulting conditions on $\underline{G}$ are

$$\left.\begin{aligned} &\text{(i)}\ \underline{G}_{AA}^{(m)} = \underline{0} \quad (m \neq 0), \\ &\text{(ii)}\ \underline{G}_{AB}^{(m)} = \underline{0} \quad (m \neq -1, 0), \\ &\qquad \underline{G}_{BA}^{(m)} = \underline{0} \quad (m \neq 0, 1), \\ &\text{(iii)}\ \underline{G}_{BB}^{(m)} = \underline{0} \quad (m \neq -1, 0, 1). \end{aligned}\right\} \tag{24}$$

From (20) and (24) we obtain the G-matrix in the partitioned form

$$\underline{G}(\theta) = \begin{pmatrix} \underline{G}_{AA}^{(0)} & , \underline{G}_{AB}^{(-1)} e^{i\theta} + \underline{G}_{AB}^{(0)} \\ \underline{G}_{BA}^{(0)} + \underline{G}_{BA}^{(1)} e^{-i\theta} & , \underline{G}_{BB}^{(-1)} e^{i\theta} + \underline{G}_{BB}^{(0)} + \underline{G}_{BB}^{(1)} e^{-i\theta} \end{pmatrix}. \tag{25}$$

It must be noticed at this point that our "nearest-neighbour coupling" assumption does represent an important restriction on the force-field of the model under consideration. First it may involve neglecting the forces opposing certain torsions of the molecule; secondly it certainly does necessitate neglect of the hydrogen-bonding in structures such as Pauling's α- and γ-helices, for these involve third- and fifth-neighbour coupling respectively.

6. APPLICATION OF PERTURBATION THEORY

The secular equation which we wish to solve is (21), in which the partitioned forms of $\underline{F}(\theta)$ and $\underline{G}(\theta)$ are given by (23) and (25). Now it has been shown in Chapter I that such a partitioned equation may be treated by perturbation theory on the assumption that the frequencies of set A are much higher than those of set B. If we consider only the high frequencies, the zeroth order approximation is found by solving the secular equation I(3a),

$$\left| \underline{G}_{AA}(\theta)\, \underline{F}_{AA}(\theta) - \lambda^{\circ}_{A}(\theta)\, \underline{I}_{A} \right| = 0,$$

which becomes, with the aid of (23) and (25),

$$\left| \underline{G}^{(0)}_{AA}\, \underline{F}^{(0)}_{AA} - \lambda^{\circ}_{A}(\theta)\, \underline{I}_{A} \right| = 0.$$

This is the secular equation for an isolated unit: every root λ°_{Ai} ($i = 1 \ldots n_A$, where n_A is the number of A-coordinates) is independent of θ. The first order correction term is then given by equation I(13), i.e.

$$\lambda^{1}_{Ai}(\theta) = \underline{x}_{Ai}\, \underline{G}_{AB}(\theta)\, \underline{F}_{BB}(\theta)\, \underline{G}_{BA}(\theta)\, \underline{x}'_{Ai}\,, \qquad (26)$$

in which $\underline{x}_{Ai}$ is that solution of the equation

$$\underline{x}_{Ai}\, \underline{G}^{(0)}_{AA}\, \underline{F}^{(0)}_{AA} = \lambda^{\circ}_{Ai}\, \underline{x}_{Ai}$$

which satisfies the normalizing condition

$$\underline{X}_{Ai}\,\underline{G}^{(0)}_{AA}\,\underline{X}'_{Ai} = 1.$$

Substituting in (26) the submatrices of (23) and (25), and using the Hermitean property of $\underline{F}$ and $\underline{G}$, we find that the correction has the form

$$\lambda^1_{Ai}(\theta) = u_i + v_i \cos\theta,$$

in which

$$u_i = \underline{X}_{Ai}\left(\underline{G}^{(0)}_{AB}\,\underline{F}^{(0)}_{BB}\,\underline{G}^{(0)}_{BA} + \underline{G}^{(-1)}_{AB}\,\underline{F}^{(0)}_{BB}\,\underline{G}^{(1)}_{BA}\right)\underline{X}'_{Ai}$$

and

$$v_i = 2\,\underline{X}_{Ai}\,\underline{G}^{(0)}_{AB}\,\underline{F}^{(0)}_{BB}\,\underline{G}^{(1)}_{BA}\,\underline{X}'_{Ai}$$

$$= 2\,\underline{X}_{Ai}\,\underline{G}^{(-1)}_{AB}\,\underline{F}^{(0)}_{BB}\,\underline{G}^{(0)}_{BA}\,\underline{X}'_{Ai}.$$

So if we take the perturbation series only as far as the first order correction, the high frequencies $\nu_{Ai}(\theta)$ are given by

$$4\pi^2\nu^2_{Ai}(\theta) = \lambda_{Ai}(\theta),$$

where

$$\lambda_{Ai}(\theta) \doteq \lambda^\circ_{Ai} + u_i + v_i\cos\theta. \qquad (27)$$

Now the allowed Raman fundamentals are obtained by putting $\theta = 0, \psi, 2\psi$ in equation (27): they are therefore

$$\lambda_{Ai}(0) \doteq \lambda^{\circ}_{Ai} + u_i + v_i ,$$

$$\lambda_{Ai}(\psi) \doteq \lambda^{\circ}_{Ai} + u_i + v_i \cos\psi ,$$

$$\lambda_{Ai}(2\psi) \doteq \lambda^{\circ}_{Ai} + u_i + v_i \cos 2\psi .$$

From these three equations, by eliminating $(\lambda^{\circ}_{Ai} + u_i)$ and v_i, we obtain a relation connecting the three sets of frequencies:

$$\lambda_{Ai}(\psi) - \tfrac{1}{2}\{\lambda_{Ai}(0) + \lambda_{Ai}(2\psi)\} \doteq \cos\psi \{\lambda_{Ai}(0) - \lambda_{Ai}(\psi)\}. \quad (28)$$

In principle at least, equation (28) provides a means by which the angle ψ of the helix may be calculated from the splitting of the variously polarized components of a high frequency Raman line.

7. DISCUSSION

The treatment in this chapter of an ideal helical molecule is intended as a starting point for an interpretation of protein spectra. But in a real protein molecule, even if (as seems likely from the experimental evidence) the structure is basically helical, it may be only the polypeptide skeleton which has helical symmetry, different side-chains (R, R′, etc.) being attached to the α carbon atoms of the various units (figure 3). We must therefore consider the probable effects of such departures from symmetry on the selection rules,

intensities and frequencies.

Obviously one effect will be a breakdown of the strict selection rules which hold when the symmetry is perfect. But it is likely that the most intense part of any band (i.e. the absorption maximum in the case of infra-red spectra) will still be that allowed by the selection rules. According to the weak coupling approximation, the intensity of any band which corresponds to a high skeletal frequency (e.g. the CO and NH frequencies) may be expected to be almost unaffected.

A more serious consequence is the effect on the frequencies. The perturbations introduced by the various side chains may be sufficiently large to invalidate the approximate formulae which have been derived. However, if the side chains are of large mass, they may be treated approximately as of infinite mass, so that the helical symmetry is effectively restored as far as the skeletal vibrations are concerned.

A few words must be said concerning the circumstances in which the approximate frequency relations are valid for a molecule with helical symmetry. First, since the formulae have been derived by perturbation theory, the frequencies concerned must be high compared with those of the rest of the molecule: in the case of a polypeptide this means that we must consider the CO stretching and the NH stretching and

bending modes. Secondly, it must be legitimate to neglect interactions, such as hydrogen bonds, which couple units other than nearest neighbours: this restriction seems to eliminate the CO and NH stretching modes of Pauling's helices, for here the CO and NH groups are connected almost collinearly through a hydrogen bond. It seems therefore that the NH bending mode is the one to which the approximate relations may best be applied.

Finally, it is perhaps important to emphasize the assumptions underlying the various sections of this chapter and to point out the consequently varying degrees of reliability which may be attached to the corresponding conclusions. The selection rules (tables 1and 2) and the secular equation (21) rest on nothing more than the helical symmetry of the molecule. The assumption of weak coupling between the units has been used to calculate the intensities (tables 1 and 2). The approximate frequency relation (28) depends on some rather special assumptions about the interactions, involving neglect of the hydrogen bonding in Pauling's helices, and on the use of first order perturbation theory in conjunction with the weak-coupling assumption. This last section is therefore somewhat less reliable than the previous sections. Even so, it is perhaps useful as an indication of the sort of approximate method which may be used in the theoretical investigation of complex helical molecules.

TABLE I

INFRA-RED SELECTION RULES AND INTENSITIES

	polarization relative to z axis	represent-ations: parameter θ	frequencies	intensities
(a)	r.h. circular (x_+)	$+\psi$	$\nu_i(\psi)$	$\frac{1}{2}f_i M_i^2 \sin^2\phi_i$
	l.h. circular (x_-)	$-\psi$		
	linear parallel (x_0)	0	$\nu_i(0)$	$f_i M_i^2 \cos^2\phi_i$
(b)	linear perpendicular (x or y)	$\pm\psi$	$\nu_i(\psi)$	$\frac{1}{2}f_i M_i^2 \sin^2\phi_i$
	linear parallel (z)	0	$\nu_i(0)$	$f_i M_i^2 \cos^2\phi_i$

TABLE 2. RAMAN SELECTION RULES AND INTENSITIES

	polarization relative to z axis		representations: parameter θ	frequencies	intensities
	incident	scattered			
(a)	r.h.circular	r.h.circular	0	$\nu_i(0)$	$g_i(a_{0i})^2$
		l.h.circular	-2ψ	$\nu_i(2\psi)$	$g_i\lvert a_{2i}\rvert^2$
		linear parallel	$-\psi$	$\nu_i(\psi)$	$g_i\lvert a_{1i}\rvert^2$
	l.h.circular	r.h.circular	2ψ	$\nu_i(2\psi)$	$g_i\lvert a_{2i}\rvert^2$
		l.h.circular	0	$\nu_i(0)$	$g_i(a_{0i})^2$
		linear parallel	ψ	$\nu_i(\psi)$	$g_i\lvert a_{1i}\rvert^2$
	linear parallel	r.h.circular	ψ	$\nu_i(\psi)$	$g_i\lvert a_{1i}\rvert^2$
		l.h.circular	$-\psi$	$\nu_i(\psi)$	$g_i\lvert a_{1i}\rvert^2$
		linear parallel	0	$\nu_i(0)$	$g_i(a'_{0i})^2$
(b)	perpendicular (x, say)	perpendicular (x)	0	$\nu_i(0)$	$g_i(a_{0i})^2$
		perpendicular (x or y)	$\pm 2\psi$	$\nu_i(2\psi)$	$\frac{1}{2}\, g_i\lvert a_{2i}\rvert^2$
		parallel (z)	$\pm\psi$	$\nu_i(\psi)$	$g_i\lvert a_{1i}\rvert^2$
	parallel (z)	perpendicular (x or y)	$\pm\psi$	$\nu_i(\psi)$	$g_i\lvert a_{1i}\rvert^2$
		parallel (z)	0	$\nu_i(0)$	$g_i(a'_{0i})^2$

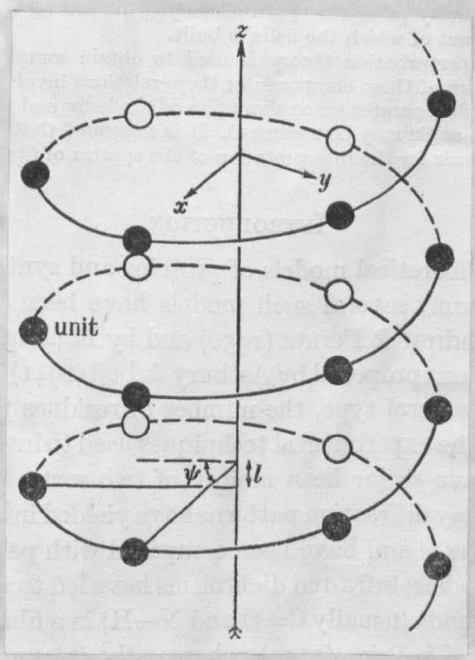

Figure 1.
Helix and coordinate axes.

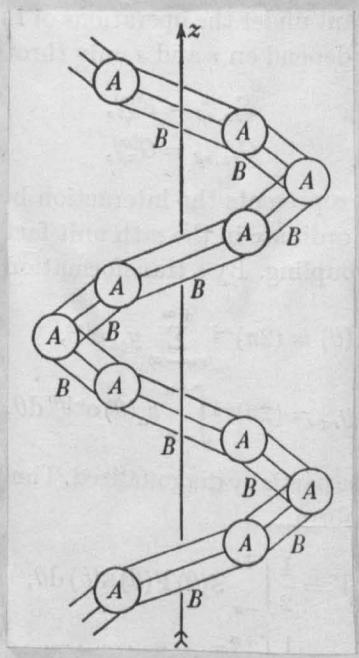

Figure 2.
System of linkages.

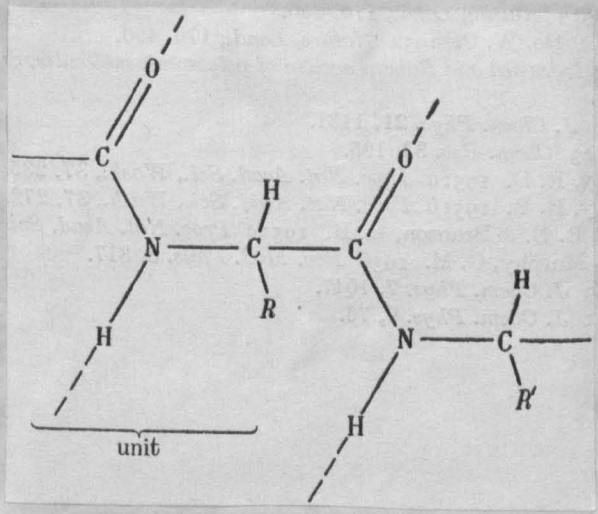

Figure 3.
Polypeptide chain; R, R′, etc. are side chains;
--- indicates hydrogen bonds.

CHAPTER IV

ON THE QUANTUM THEORY OF UNIMOLECULAR REACTION RATES.

Summary.

A theory of unimolecular reaction rates is discussed which is a quantum mechanical generalization of the classical theory developed by N. B. Slater. It is shown that under normal laboratory conditions the theory leads to a rate in excess of the classical value, but the formula obtained cannot be made to fit the available experimental data without using unreasonable values of the parameters. Moreover, a non-vanishing rate at the absolute zero of temperature is predicted.

It is pointed out that similar predictions are to be expected of any quantal theory which adopts Slater's critical configuration criterion for dissociation, and the need for a careful analysis of the process of dissociation is stressed.

I. INTRODUCTION

In the current theory of unimolecular reactions developed by Slater (1948, 1953a) a polyatomic molecule is treated as a classical vibrating system which dissociates when a certain

internal coordinate r, the reaction coordinate, exceeds a critical value r_0. It is assumed that for $r < r_0$ the potential energy is quadratic in the coordinates and that

$$L \ll \nu, \tag{1}$$

where L is the average frequency with which r attains the value r_0 in a sufficiently energized molecule and ν is a certain mean vibration frequency. If in addition

$$L \ll \nu_{coll} \ll \nu, \tag{2}$$

where ν_{coll} is the mean collision frequency in a gas of the molecules, it is found that the reaction rate is given by

$$K = \nu \exp(-E_0/kT), \tag{3}$$

in which E_0, the activation energy, is the minimum energy needed by a molecule in order to reach $r = r_0$. The conditions (1) and (2) are fulfilled by molecules with ten or more internal degrees of freedom (i.e. with more than five atoms) at ordinary pressures; at lower pressures, where the collision frequency no longer satisfies condition (2), the reaction is no longer of the first order and a more complicated expression is found for the rate K.

Comparison of the predictions of this theory with experimental data on the isomerization of cyclopropane (Slater,

1953b) shows that, although the way in which K varies with pressure is accounted for satisfactorily, the predicted values of K are in general too small. Moreover, from the theoretical standpoint there is one major defect of the theory which may well be responsible for its failure to predict K absolutely: a classical treatment of vibrations is in general valid only if $\nu \ll kT/h$, a condition which is certainly not satisfied by most molecular vibration frequencies at ordinary temperatures. The aim of this chapter is to discuss the theory of unimolecular reaction rates from a point of view which resembles that of Slater as closely as possible apart from the substitution of quantum mechanics for classical mechanics. The resulting expression for K once again has some unsatisfactory features (in particular, a non-zero rate at T=0 is predicted), and it is evident on careful consideration of the assumptions used that certain simplifications which were justifiable in the classical theory are no longer justifiable in the quantum theory. The removal of these simplifications appears to be a matter of some difficulty and has not yet been achieved; nevertheless, the theory as it stands is presented here in the hope that the mathematical techniques employed may be of use in future developments.

First of all, in section 2 the dissociation of a molecule with only one vibrational coordinate is treated

classically by the method of Slater (1948). Next, in section 3 the quantum mechanical density matrix formalism is described, and in section 4 this method is applied to the problem treated classically in section 2. Although in the laboratory the condition (2) is never fulfilled by such a molecule, it is useful to deal with this simplest problem first since it provides a clear illustration of the differences between the classical and quantum theoretical results without the additional complications which arise from multiple vibrations.

The general theory of the dissociation of a polyatomic molecule is developed in section 5. Finally, section 6 consists of a discussion of the results obtained and an examination of the assumptions involved. The derivation of certain formulae occurring in the text is carried out in the mathematical appendices.

2. THE DISSOCIATION OF A SIMPLE OSCILLATOR: CLASSICAL THEORY.

The equations governing the course of a unimolecular dissociation are

$$\left.\begin{aligned} -dN/dt &= KN - K'N'^2, \\ -dN'/dt &= K'N'^2 - KN, \end{aligned}\right\} \qquad (4)$$

where KN is the average frequency of dissociation and $K'N'^2$ that of association in an assembly of N associated and N'

dissociated molecules: K and K', thus defined, are the reaction rates for dissociation and association respectively. Chemical equilibrium is reached when

$$N'^2/N = K/K' :$$

this quantity is the equilibrium constant for the reaction.

The model of dissociation discussed by Slater (1948) is most simply described for a molecule possessing only one vibrational coordinate, that is, for a diatomic molecule. The potential energy V for relative motion of the nuclei of such a system is known to have the following general form as a function of q, the amount by which the bond length exceeds its equilibrium value: when q is small, $V = \frac{1}{2}Fq^2$, where F is the force constant of the bond; when q is large and positive, $V \longrightarrow E_0$ asymptotically, where E_0 is the dissociation energy of the molecule referred to the equilibrium configuration as zero. It is reasonable to join up the curves $V = \frac{1}{2}Fq^2$ and $V = E_0$ into the full curve of figure 1 as a first approximation to the complete potential and to take as the criterion for dissociation the exceeding by q of the critical value q_0, given by

$$E_0 = \tfrac{1}{2}Fq_0^2 \qquad (5)$$

at which the curves meet: for, according to classical mechanics, a molecule with sufficient kinetic energy to

vibrate as far as q_0 and with a positive relative velocity ($\dot{q} > 0$) will continue to move with constant $\dot{q}$ until eventually the constituent nuclei are infinitely separated.

To calculate the rate K one considers a hypothetical statistical ensemble of associated molecules in thermal equilibrium amongst themselves at absolute temperature T. The distribution of systems in phase space corresponding to this quasi-equilibrium is taken to be that appropriate to the potential $V = \frac{1}{2}Fq^2$ (for $q > q_0$ the broken curve of figure 1): the distribution function is therefore

$$f_c(p,q) = A \exp(-\beta H), \tag{6}$$

in which $\beta = (kT)^{-1}$, where k is Boltzmann's constant, and the Hamiltonian is given by

$$H(p,q) = \tfrac{1}{2} p^2/m + \tfrac{1}{2} Fq^2, \tag{7}$$

where m is the reduced mass of the system and $p = m\dot{q}$ is the momentum canonically conjugate to q. The interpretation of f_c is that $f_c(p,q)\,dp\,dq$ is the average number of systems in the region (p,q) to (p + dp, q + dq), the total number being

$$\int_{-\infty}^{+\infty}\int f_c(p,q)\,dpdq = N. \tag{8}$$

The average frequency with which $q = q_0$ is crossed by systems with $\dot{q} > 0$ is

$$\int_0^{\infty} (p/m)\ f_c(p,q_0)\,dp : \tag{9}$$

these are the systems which dissociate, so the expression (9) is the contribution to $(-dN/dt)$ from dissociation. Comparing (4), (8) and (9) we see that the rate is

$$K = \int_0^\infty (p/m)\ f_c(p,q_0)\ dp \Big/ \iint_{-\infty}^{+\infty} f_c(p,q)\ dpdq. \quad (10)$$

With the aid of (6) and (7) we obtain on performing the integrations

$$K = (2\pi)^{-1} (F/m)^{\frac{1}{2}} \exp(-\tfrac{1}{2}\beta F q_0^2);$$

this expression is just Slater's formula (3), in which now $\nu = (2\pi)^{-1} (F/m)^{\frac{1}{2}}$, the molecular vibration frequency, and the activation energy E_0 is just the dissociation energy already defined by (5).

Equation (10) may be rewritten in a way which will prove useful in the quantum theory:

$$K = j_+(q_0) \Big/ \int_{-\infty}^{+\infty} n(q)\ dq, \quad (11)$$

where $j_+(q_0)$ is the current of systems with positive velocity $\dot{q}$ across $q = q_0$ and $n(q)$ is the spatial density of associated systems. Classically,

$$j_+(q) = \int_0^\infty (p/m)\ f_c(p,q)\ dp$$

and $n(q) = \int_{-\infty}^{+\infty} f_c(p,q)\ dp$;

we require the quantum mechanical analogues of these expressions.

3. THE QUANTUM MECHANICAL DENSITY MATRIX

In the quantum mechanical description of a statistical ensemble it is no longer convenient to use a phase space formulation: indeed although it is possible (as is shown in Appendix B) to find a function $f_e(p,q)$ which has many of the properties of f_c and which tends to f_c as $h \longrightarrow 0$, the Heisenberg uncertainty principle indicates that the interpretation of f_e as a distribution function in p and q simultaneously is no longer permissible. The formulation which is most convenient employs the Schrödinger representation of the density matrix first introduced by von Neumann (1932).

A system in a pure state - one in which a maximal set of conditions is imposed on the dynamic variables - may be described by means of a Schrödinger function $\psi(q,t)$, from which all information about the state may be derived. In particular, if ψ is normalized ($\int_{-\infty}^{+\infty} \psi^* \psi \, dq = 1$), the probability that a measurement of the coordinate will yield a value in the range $(q, q + dq)$ is $P(q,t)\,dq$, where

$$P(q,t) = \psi^* \psi , \qquad (12)$$

and the probability current, that is, the rate of increase of the probability that the coordinate value exceeds q is

$$J(q,t) = \tfrac{1}{2} i\hbar m^{-1} (\psi \, \partial\psi^*/\partial q - \psi^* \, \partial\psi/\partial q): \qquad (13)$$

P and J satisfy the equation expressing conservation of

probability,

$$\partial P/\partial t + \partial J/\partial q = 0,$$

provided that ψ satisfies the Schrödinger equation

$$i\hbar\,\partial\psi/\partial t = H(-i\hbar\partial/\partial q, q)\,\psi. \qquad (14)$$

Any state of an ensemble is completely specified by a density matrix $\rho(q',q'';t)$ which has the following properties: at any given instant, say $t = 0$, ρ may be written in the form

$$\rho(q',q'';0) = \sum_\alpha \rho_\alpha \psi_\alpha(q')\,\psi_\alpha^*(q''),$$

in which $\psi_\alpha(q)$ is a normalized eigenfunction of some complete set of commuting dynamic variables, ρ_α is the expectation value of the number of systems in the pure eigenstate α and the summation is over all such eigenstates. Provided that there is only negligible interaction between the systems, the members of each sub-ensemble α move according to the Schrödinger equation (14), so at a general time t

$$\rho(q',q'';t) = \sum_\alpha \rho_\alpha \psi_\alpha(q',t)\,\psi_\alpha^*(q'',t), \qquad (15)$$

in which $\psi_\alpha(q,t)$ is the solution of (14) such that

$$\psi_\alpha(q,0) = \psi_\alpha(q):$$

thus the equation of motion for the density matrix is

$$i\hbar\,\partial\rho/\partial t = (H'-H'')\,\rho,$$

where $H' = H(-i\hbar\partial/\partial q', q')$, etc.

The quantities P and J may be generalized in a fairly obvious manner: according to equations (12) and (15) the number of systems expected to lie in the range $(q, q + dq)$ is is $n(q, t)\,dq$, where

$$n(q, t) = \sum_\alpha \rho_\alpha P_\alpha$$
$$= \rho(q, q; t); \qquad (16)$$

similarly, from (13) and (15) the expected rate at which systems exceed the coordinate value q (i.e. the current) is

$$j(q, t) = \sum_\alpha \rho_\alpha J_\alpha$$
$$= \tfrac{1}{2} i\hbar m^{-1} (\partial\rho/\partial q'' - \partial\rho/\partial q')_{q'=q''=q}. \qquad (17)$$

It follows from the last three equations that n and j obey the equation expressing conservation of systems,

$$\partial n/\partial t + \partial j/\partial q = 0.$$

An ensemble in thermal equilibrium is characterized by a Boltzmann distribution of systems amongst the energy eigenstates, that is to say, in (15) the Schrödinger functions have the form,

$$\psi_\alpha(q, t) = \psi_\alpha(q) \exp(E_\alpha t/i\hbar),$$

where $\psi_\alpha(q)$ is the eigenfunction of H belonging to the eigen-

value E_α, and the weight factors are given by

$$\rho_\alpha = A \exp(-\beta E_\alpha),$$

where A is determined by the size of theensemble. The quantity we wish to calculate (K) is independent of the size of the ensemble, so it is convenient to set A = 1: then the density matrix, now constant in time, becomes

$$\rho_e(q',q'';\beta) = \sum_\alpha \exp(-\beta E_\alpha)\,\psi_\alpha(q')\,\psi_\alpha^*(q''). \quad (18)$$

Since $\psi_\alpha(q)$ satisfies the equation

$$H\psi_\alpha = E_\alpha \psi_\alpha$$

and the set of functions has the completeness property

$$\sum_\alpha \psi_\alpha(q')\,\psi_\alpha^*(q'') = \delta(q'-q''),$$

where $\delta(x)$ is Dirac's delta function, it follows that the equilibrium density matrix is that solution of the Bloch equation

$$H'\rho_e = -\partial\rho_e/\partial\beta = H''\rho_e \quad (19)$$

which satisfies the boundary condition

$$\rho_e(q',q'';0) = \delta(q'-q'')$$

and is otherwise well behaved.

The total number of systems in an ensemble is, from (16), the trace of the density matrix:

$$N = \int_{-\infty}^{+\infty} n(q,t)\,dq = \int_{-\infty}^{+\infty} \rho(q,q;t)\,dq.$$

In the special equilibrium ensemble with A = 1 it turns out to be identical with the partition function:

$$N = \sum_{\alpha} \exp(-\beta E_{\alpha}) \int_{-\infty}^{+\infty} \psi_{\alpha}(q)\, \psi_{\alpha}^{*}(q)\, dq$$
$$= Z(\beta), \qquad (20)$$

since the Schrödinger functions are normalized.

4. THE DISSOCIATION OF A SIMPLE OSCILLATOR: QUANTUM THEORY

We now have the general quantum theoretical expressions (16) and (17) for density and current and, proceeding as in section 2, we expect K to be of the form $j(q_0)/N$, where j is to be calculated for an equilibrium ensemble of simple harmonic oscillators. However, in any equilibrium ensemble j turns out to be zero, since from (13) J vanishes for any state (such as an eigenstate of H) which may be described by a real $\psi(q)$. Inspection of (11) shows that what we actually want to find is not j but j_+, the current of systems with positive velocity.

The Schrödinger function $\psi(q)$ describing any pure state of a system may be analysed into plane waves, $\exp(ipq/\hbar)$, which describe eigenstates of the momentum corresponding to eigenvalues p, as follows:

$$\psi(q) = (2\pi\hbar)^{-\frac{1}{2}} \int_{-\infty}^{+\infty} \phi(p) \exp(ipq/\hbar)\, dp.$$

By Fourier's integral theorem the "momentum wave function" $\phi(p)$ is given by

$$\phi(p) = (2\pi\hbar)^{-\frac{1}{2}} \int_{-\infty}^{+\infty} \psi(q) \exp(-ipq/\hbar)\, dq. \quad (21)$$

The part of ψ which corresponds to states of positive momentum (or velocity) only is therefore the function

$$\psi_+(q) = (2\pi\hbar)^{-\frac{1}{2}} \int_0^{\infty} \phi(p) \exp(ipq/\hbar)\, dp:$$

this expression may be transformed by means of (21) into the form

$$\psi_+(q) = \int_{-\infty}^{+\infty} \psi(x)\, \delta_+(x-q)\, dx, \quad (22)$$

in which

$$\delta_+(x) = \tfrac{1}{2}\delta(x) + (2\pi i x)^{-1}. \quad (23)$$

Similarly the negative momentum part of ψ is the function

$$\psi_-(q) = \int_{-\infty}^{+\infty} \psi(x)\, \delta_-(x-q)\, dx,$$

where $\delta_- = \delta_+^*$. When ψ is real, as in an eigenstate of H, $\psi_- = \psi_+^*$ and it is easily shown that the expression (13) for the total current splits up into two parts:

$$J = J_+ + J_-,$$

where J_+, J_- are obtained from (13) by substituting ψ_+, ψ_-

respectively for ψ.

The generalization to the equilibrium ensemble follows immediately from equations (15), (17) and (22): the formula for the current of systems with positive velocity is

$$j_+(q) = \tfrac{1}{2}\, i\hbar m^{-1} \left(\partial\rho_+/\partial q'' - \partial\rho_+/\partial q'\right)_{q'=q''=q}, \qquad (24)$$

where

$$\rho_+(q',q';\beta) = \int_{-\infty}^{+\infty}\int \rho_e(x',x'';\beta)\,\delta_+(x'-q')\,\delta_+^*(x''-q'')\,dx'\,dx''. \qquad (25)$$

Further manipulation of equations (23) to (25) leads to the simpler result

$$j_+(q) = (4\pi m)^{-1}\hbar\left\{\phi''(q,q) - \phi'(q,q)\right\}, \qquad (26)$$

in which

$$\left.\begin{aligned} &\phi' = \partial\phi/\partial q', \quad \phi'' = \partial\phi/\partial q'' \\ &\text{and} \\ &\phi(q',q'') = \int_{-\infty}^{+\infty} \rho_e(\xi+q',q'';\beta)\,\xi^{-1}\,d\xi. \end{aligned}\right\} \qquad (27)$$

All that remains now is to evaluate j_+ and N for the simple harmonic oscillator. It is shown in Appendix A that the equilibrium density matrix for such a system is given by

$$\rho_e(q',q'';\beta) = (b/2\pi)^{\frac{1}{2}} \exp\left\{-\tfrac{1}{2}a(q'^2+q''^2) + bq'q''\right\}, \qquad (28)$$

in which

$$\left.\begin{aligned} a &= 4\pi^2 m h^{-1}\nu\, \coth(h\nu\beta), \\ b &= 4\pi^2 m h^{-1}\nu\, \operatorname{cosech}(h\nu\beta). \end{aligned}\right\} \qquad (29)$$

The quantities defined in (27) may be calculated successively from the expression (28):

$$\phi(q',q'') = (b/2\pi)^{\frac{1}{2}} \exp\{-\tfrac{1}{2}a^{-1}(a^2-b^2)q''^2\} \int_{-\infty}^{+\infty} \exp\{-\tfrac{1}{2}a(\xi+q'-a^{-1}bq'')^2\}\xi^{-1}d\xi,$$

$$\phi'(q',q'') = (-aq'+bq'')\,\phi(q',q'') - a(b/a)^{\frac{1}{2}} \exp\{-\tfrac{1}{2}a^{-1}(a^2-b^2)q''^2\},$$

$$\phi''(q',q'') = (bq'-aq'')\,\phi(q',q'') + b(b/a)^{\frac{1}{2}} \exp\{-\tfrac{1}{2}a^{-1}(a^2-b^2)q''^2\}.$$

By substituting these quantities into (26) we obtain for the current the formula

$$j_+(q) = (4\pi m)^{-1}\hbar(a+b)(b/a)^{\frac{1}{2}} \exp\{-\tfrac{1}{2}a^{-1}(a^2-b^2)q^2\}. \quad (30)$$

The total number of systems is, from (16) and (28),

$$N = \{b/2(a-b)\}^{\frac{1}{2}}. \quad (31)$$

(According to (20) and (29) this is in fact just the usual oscillator partition function,

$$Z(\beta) = \{2\sinh(\tfrac{1}{2}h\nu\beta)\}^{-1}.)$$

Finally, by combining (11), (30) and (31) we obtain for the dissociation rate

$$K = (4\pi m)^{-1}\hbar(a+b)\{2(a-b)/a\}^{\frac{1}{2}} \exp\{-\tfrac{1}{2}a^{-1}(a^2-b^2)q_0^2\},$$

an expression which, with the aid of (5) and (29), may be

written explicitly in the form

$$K(T) = \nu\{1+\tanh^2(h\nu/2kT)\}^{-\frac{1}{2}} \exp\{-(E_0/h\nu)\tanh(h\nu/kT)\}. \quad (32)$$

General behaviour of K(T):

By setting h = 0 in (32) we obtain once more Slater's classical value

$$K_c = \nu \exp(-E_0/kT),$$

as is to be expected: the classical formula provides a good approximation to K whenever $h\nu/kT$ is small, that is, at high temperatures and low frequencies. As $T \to \infty$, both classical and quantum rates approach the upper limit

$$K(\infty) = \nu.$$

At the other extreme, as $T \to 0$, although $K_c \to 0$ the quantum rate tends to the finite lower limit

$$K(0) = (\nu/\sqrt{2}) \exp(-E_0/h\nu).$$

Between these limits both rates increase monotonically with T.

Let us write $\kappa = K/K_c$, $\theta = kT/E_0$, $\alpha = h\nu/E_0$, the last quantity being what would be a measure of the anharmonicity if we were using a Morse potential: then from (32)

$$\kappa = \{1+\tanh^2(\tfrac{1}{2}\alpha\theta^{-1})\}^{-\frac{1}{2}} \exp\{\theta^{-1} - \alpha^{-1}\tanh(\alpha\theta^{-1})\}.$$

The asymptotic behaviour of κ as $\theta \to \infty$ is found by expanding this expression as a Taylor series in θ^{-1}:

$$K = 1 - \tfrac{1}{8}\alpha^2\theta^{-2} + \tfrac{1}{3}\alpha^2\theta^{-3} + O(\alpha^4\theta^{-4}). \qquad (33)$$

It appears that at very high temperatures $K < K_0$. But since $K(0) > K_0(0)$ there must in general be some critical temperature T^* at which $K = K_0$ (see figure 2); in particular, if α is small this temperature may be found from the expansion (33), regarded as a power series in α, by setting $K = 1$: it is given by $\theta^* = 8/3$, that is

$$T^* = 8E_0 / 3k. \qquad (34)$$

5. DISSOCIATION OF A POLYATOMIC MOLECULE: QUANTUM THEORY.

In general the displacement of a polyatomic molecule from its equilibrium configuration may be specified by a column matrix $\underline{q}$ of internal coordinates (bond extensions, angular deformations, etc.), in terms of which the potential and internal kinetic energies are given by the quadratic expressions

$$V = \tfrac{1}{2}\,\underline{\tilde{q}\,F\,q},$$

$$T = \tfrac{1}{2}\,\underline{\tilde{\dot{q}}\,G^{-1}\,\dot{q}},$$

provided that the distortion is not too large. The symmetric matrices $\underline{F}$ and $\underline{G}$ are those defined in the General Introduction. It is convenient to define normal coordinates $\underline{Q}$ by the transformation

$$\underline{q} = \underline{N}\underline{Q}, \qquad (35)$$

where the square matrix $\underline{N}$ is such that

$$\underline{\tilde{N}}\,\underline{G^{-1}}\,\underline{N} = \underline{I},$$

$$\underline{\tilde{N}}\,\underline{F}\,\underline{N} = \underline{\Lambda} = \text{diag.}\ (4\pi^2\nu_\alpha^2),$$

in which ν_α is a classical vibration frequency calculated from the equation

$$|\underline{GF} - 4\pi^2\nu_\alpha^2\underline{I}| = 0.$$

(This definition differs slightly from that used by Slater.) It follows that the Hamiltonian

$$H(\underline{p},\underline{q}) = \tfrac{1}{2}\,\underline{\tilde{p}}\,\underline{G}\,\underline{p} + \tfrac{1}{2}\,\underline{\tilde{q}}\,\underline{F}\underline{q},$$

in which $p_r = \partial T/\partial \dot{q}_r$, may be expressed as a simple sum of squares in terms of normal coordinates:

$$H(\underline{P},\underline{Q}) = \tfrac{1}{2}\,\underline{\tilde{P}}\,\underline{P} + \tfrac{1}{2}\,\underline{\tilde{Q}}\,\underline{\Lambda}\,\underline{Q}. \qquad (36)$$

Moreover, if f(z) is any single-valued function which may be expanded as a series in integral powers of z, we may write

$$\underline{N}\,f(\underline{\Lambda})\,\underline{\tilde{N}} = f(\underline{GF})\,\underline{G}. \qquad (37)$$

Let us assume that dissociation can occur because V becomes independent of a certain internal coordinate r (the reaction coordinate) when r is large. As before, we shall take a model in which V changes abruptly from the parabolic well to the parabolic trough form at a critical distortion r_0. We suppose that r is some linear combination of the q s,

$$r = \underline{l}\,\underline{q}, \qquad (38)$$

so that the critical surface $r = r_0$ is a plane in q-space (see figure 3). The criterion for dissociation is then

$r > r_0$, and to find the rate we have to calculate the outward current of systems across the surface $\underline{1q} = r_0$ in an ensemble of undissociated molecules in thermal equilibrium. Indeed, by an obvious generalization of (11), the rate is given by

$$K = \int \underline{j}_+ \, \underline{dS} \; / \int n \, d\tau, \tag{39}$$

where $\underline{j}_+$ is the current density vector of systems with outward $\dot{r}$, n the total number density, $\underline{dS}$ the surface element of $\underline{1q} = r_0$ and $d\tau$ the volume element of q-space.

Once again it is convenient to employ the density matrix defined by equation (15), where now the Schrödinger functions depend on all the qs. In terms of $\rho(\underline{q'}, \underline{q''}; t)$ we have as the generalizations of (16) and (17) the number density

$$n(\underline{q}, t) = \rho(\underline{q}, \underline{q}; t) \tag{40}$$

and the current density vector

$$\underline{j}(\underline{q}, t) = \tfrac{1}{2} i\hbar \, \underline{G} \left(\partial\rho/\partial\underline{q''} - \partial\rho/\partial\underline{q'}\right)_{\underline{q'}=\underline{q''}=\underline{q}}. \tag{41}$$

The equilibrium density matrix $\rho_e(\underline{q'}, \underline{q''}; \beta)$ now satisfies the Bloch equation (19) and the boundary condition

$$\rho(\underline{q'}, \underline{q''}; 0) = \delta(\underline{q'} - \underline{q''}).$$

According to (36) the Hamiltonian may be written in terms of normal coordinates as the sum of simple oscillator terms

$$H(\underline{P}, \underline{Q}) = \sum_\alpha \left(\tfrac{1}{2} P_\alpha^2 + 2\pi^2 \nu_\alpha^2 Q_\alpha^2\right):$$

it follows that $\rho_e(\underline{Q'}, \underline{Q''}; \beta)$ reduces to the product of simple oscillator factors

$$\rho_e(\underline{Q'}, \underline{Q''}; \beta) = \prod_\alpha \rho_e(Q'_\alpha, Q''_\alpha; \beta)$$
$$= \left\{\prod_\alpha (b_\alpha/2\pi)^{1/2}\right\} \exp\left\{-\tfrac{1}{2}\sum_\alpha a_\alpha (Q'^2_\alpha + Q''^2_\alpha) + \sum_\alpha b_\alpha Q'_\alpha Q''_\alpha\right\},$$

where

$$\left.\begin{aligned} a_\alpha &= 4\pi^2 h^{-1} \nu_\alpha \coth(h\nu_\alpha \beta), \\ b_\alpha &= 4\pi^2 h^{-1} \nu_\alpha \operatorname{cosech}(h\nu_\alpha \beta). \end{aligned}\right\} \tag{42}$$

To evaluate the component of $\underline{j}$ normal to $\underline{lq} = r_0$ we introduce an orthogonal transformation of the Qs,

$$\underline{x} = \underline{TQ} \quad (\underline{T}\tilde{\underline{T}} = \underline{I}), \tag{43}$$

such that $x_1 \propto r$: from (35), (37), (38) and (43), the first row of $\underline{T}$ must be given by

$$\underline{T}_1 = (\underline{l}\,\underline{NN}\tilde{\underline{l}})^{-\frac{1}{2}}\,\underline{l}\,\underline{N}$$
$$= (\underline{l}\,\underline{G}\,\tilde{\underline{l}})^{-\frac{1}{2}}\,\underline{l}\,\underline{N}, \tag{44}$$

and the critical value of x_1 by

$$x_0 = (\underline{l}\,\underline{G}\,\tilde{\underline{l}})^{-\frac{1}{2}}\, r_0. \tag{45}$$

Then, from (41), in the new coordinates the normal component is just

$$j_1 = \tfrac{1}{2}\, i\hbar\, (\partial\rho_e/\partial x''_1 - \partial\rho_e/\partial x'_1)_{\underline{x}' = \underline{x}'' = \underline{x}}, \tag{46}$$

in which

$$\rho_e(\underline{x'}, \underline{x''}; \beta) = \rho_e(\underline{Q'}, \underline{Q''}; \beta)$$
$$= |\underline{B}/2\pi|^{\frac{1}{2}} \exp\left\{-\tfrac{1}{2}(\tilde{\underline{x}}'\underline{A}\underline{x}' + \tilde{\underline{x}}''\underline{A}\underline{x}'') + \tilde{\underline{x}}'\underline{B}\underline{x}''\right\} \tag{47}$$

where, according to (42) and (43),

$$\underline{A} = \underline{T}\ \text{diag.}\ (a_\alpha)\ \underline{\tilde{T}},$$
$$\underline{B} = \underline{T}\ \text{diag.}\ (b_\alpha)\ \underline{\tilde{T}}. \qquad (48)$$

But in calculating K we require not j_1 but j_{1+}, the part of the current density corresponding to positive velocities $\dot{x}_1$. The analysis of section 4 shows that this quantity is given by (46) with ρ_e replaced by ρ_+, defined by the integral

$$\rho_+(\underline{x',x''};\beta) = \int_{-\infty}^{+\infty}\rho_e(x'x'_2\cdots x'_n, x''x''_2\cdots x''_n;\beta)\,\delta_+(x'-x'_1)\,\delta_+^*(x''-x''_1)\,dx'dx''. \qquad (49)$$

Substituting from equations (46) to (49) into (39) and rearranging the integrals by the method used in section 4, we find for the rate the expression

$$K = (\hbar/4\pi Z)\{\phi''(x_0,x_0) - \phi'(x_0,x_0)\}, \qquad (50)$$

where now

$$\phi'(x'_1,x''_1) = \partial\phi/\partial x'_1,$$
$$\phi''(x'_1,x''_1) = \partial\phi/\partial x''_1,$$
$$\phi(x'_1,x''_1) = \int_{-\infty}^{+\infty}\sigma(x,x''_1)(x-x'_1)^{-1}\,dx,$$
$$\sigma(x'_1,x''_1) = \int_{-\infty}^{+\infty}\cdots\int\rho_e(x'_1x_2\cdots x_n, x''_1x_2\cdots x_n)\,dx_2\cdots dx_n \qquad (51)$$

and, by (40) and (47),

$$Z(\beta) = \int_{-\infty}^{+\infty}\cdots\int\rho_e(\underline{x,x};\beta)\,dx_1\cdots dx_n$$
$$= \left|\tfrac{1}{2}\underline{B}(\underline{A}-\underline{B})^{-1}\right|^{\frac{1}{2}}. \qquad (52)$$

The integrations in (51) are performed after expressing all matrices in partitioned form, according to the scheme

$$\underline{x} = \begin{pmatrix} x_1 \\ \underline{x}_2 \end{pmatrix}.$$

Then we write

$$\varrho_e(x_1' x_2 \cdots x_n, x_1'' x_2 \cdots x_n) = |\underline{B}/2\pi|^{\frac{1}{2}} \exp\left\{-\tfrac{1}{2}(\tilde{\underline{x}}_2 \underline{\alpha} \underline{x}_2 + 2\underline{\beta}\underline{x}_2 + \gamma)\right\},$$

in which

$$\underline{\alpha} = \underline{C}_{22},$$

$$\underline{\beta} = \tfrac{1}{2}\underline{C}_{12}(x_1' + x_1''),$$

$$\gamma = A_{11}(x_1' - x_1'')^2 + C_{11} x_1' x_1''$$

and

$$\underline{C} = 2(\underline{A} - \underline{B}). \tag{53}$$

On integrating we obtain

$$\sigma(x_1', x_1'') = |\underline{B}/2\pi|^{\frac{1}{2}} |\underline{\alpha}/2\pi|^{-\frac{1}{2}} \exp\left\{-\tfrac{1}{2}(\gamma - \underline{\beta}\underline{\alpha}^{-1}\tilde{\underline{\beta}})\right\},$$

which may be rewritten with the aid of (52) and (53) in the form

$$\sigma(x_1', x_1'') = Z\left(|\underline{C}|/2\pi|\underline{C}_{22}|\right)^{\frac{1}{2}} \exp\left\{-\tfrac{1}{2}u(x_1'^2 + x_1''^2) + v x_1' x_1''\right\}, \tag{54}$$

where

$$u = A_{11} - \tfrac{1}{2}\underline{C}_{12}\underline{C}_{22}^{-1}\underline{C}_{21},$$

$$v = A_{11} - \tfrac{1}{2}C_{11} + \tfrac{1}{2}\underline{C}_{12}\underline{C}_{22}^{-1}\underline{C}_{21}.$$

The calculation of K from (50) and (54) proceeds as in

section 4 and leads to the expression

$$K = (\hbar/2\pi) E_{11} \{A_{11} D_{11} - \tfrac{1}{4}(C_{11} D_{11} - 1)\}^{-\frac{1}{2}} \exp\left\{-\tfrac{1}{2} x_0^2 E_{11} [A_{11} D_{11} - \tfrac{1}{4}(C_{11} D_{11} - 1)]^{-1}\right\}, \quad (55)$$

in which

$$\left.\begin{aligned} \underline{D} &= \underline{C}^{-1} = \tfrac{1}{2}(\underline{A} - \underline{B})^{-1}, \\ \underline{E} &= \tfrac{1}{2}(\underline{A} + \underline{B}). \end{aligned}\right\} \quad (56)$$

The expression (55) gives K in terms of the coordinates $\underline{x}$; it may be expressed in terms of the original system $\underline{q}$ by transforming the 11-elements of the various matrices defined in (42), (48), (53) and (56) with the aid of the relations (37), (44) and (45): the final result has the form

$$K = \{\langle\theta\rangle / 2\pi\hbar\beta\mu^{\frac{1}{2}}\} \exp\{-r_0^2 \langle\theta\rangle / 2\hbar^2 \beta\mu\}, \quad (57)$$

where

$$\mu = \langle\phi\rangle\langle\chi\rangle - \tfrac{1}{4}\{\langle\phi\rangle\langle\psi\rangle - \langle 1\rangle^2\},$$

in which the notation

$$\langle f\rangle = \underline{1}\, f(\hbar^2\beta^2 \underline{GF})\, \underline{G}\, \underline{\tilde{1}}$$

is employed, and

$$\theta(z) = \tfrac{1}{2} z^{\frac{1}{2}} \coth(\tfrac{1}{2} z^{\frac{1}{2}}),$$

$$\phi(z) = z^{-1}\theta(z),$$

$$\chi(z) = z^{\frac{1}{2}} \coth(z^{\frac{1}{2}}),$$

$$\psi(z) = z/\theta(z).$$

(N.B. $\langle 1\rangle = \underline{1}\,\underline{G}\,\underline{\tilde{1}}$.)

The Classical Limit:

It is easily shown that as $\hbar \to 0$ the expression (57)

approaches the limit

$$K_c = \{\underline{1}\tilde{G}\underline{1}/4\pi^2\underline{1}\tilde{F}^{-1}\underline{1}\}^{\frac{1}{2}} \exp\{-\tfrac{1}{2}\beta r_o^2/\underline{1}\tilde{F}^{-1}\underline{1}\}. \qquad (58)$$

Now the first factor is just a generalization of the mean frequency ν associated with the reaction coordinate, which Slater defined in his 1948 paper (equation 12) and it is shown in Appendix C that the dissociation energy is given by

$$E_o = r_o^2/2\,\underline{1}\,F^{-1}\underline{1}\,. \qquad (59)$$

So (58) reduces once more to Slater's formula

$$K_c = \nu \exp(-E_o/kT).$$

6. DISCUSSION

The general result (57) is rather too complicated to admit of a simple interpretation, so it is perhaps best to restrict the discussion to the simpler one-dimensional expression (32). One feature of this formula is that under normal laboratory conditions it predicts a rate in excess of the classical value. For example, if we take the values of the activation energy E_o and mean frequency ν used by Slater (1953b, pp.234, 236) for cyclopropane, we find that the parameter α ($= h\nu/E_o$) is small (about 0.05), so the critical temperature T^*, below which $K > K_c$, may be calculated from (34): it turns out to be 87,000°C. This is gratifying, for it appears to be a characteristic of Slater's theory that

its predictions fall short of the measured rates. However, an actual calculation shows that the experimental data on cyclopropane (Chambers & Kistiakowsky, 1934) cannot be fitted by the formula (32) unless an entirely unreasonable value is assigned to ν.

Furthermore, the prediction by (32) of a non-vanishing rate at T = 0 is very disturbing: it implies that a molecule in its vibrational ground state is capable of dissociating, a suggestion which seems to be at variance with what one usually understands by dissociation. It must be emphasized here that any quantum theoretical treatment which adopts Slater's critical configuration criterion for dissociation must lead to a similar conclusion: for it is merely a consequence of the fact that even bound-state wave functions extend into regions of configuration space which classically are forbidden to a molecule with so little energy. Thus it appears that a prerequisite of any satisfactory quantum theory of unimolecular dissociation is a careful analysis of what is really meant by the statement that a molecule is in a dissociated state.

APPENDIX A

The density matrix $\rho_\alpha(q', q''; \beta)$ may be calculated directly from equation (18) if the eigenfunctions $\psi_\alpha(q)$ are

already known: for the harmonic oscillator this procedure entails a summation over Hermite polynomials. Alternatively one might attempt to solve the Bloch equation with the appropriate boundary condition. There is however a third method which is particularly tractable when applied to the oscillator problem: it was first used for this purpose by Kennard (1927) and Bloch (1932). This method utilizes a formal similarity between $\rho_e(q', q''; \beta)$ and $S(q', q''; t)$, the Green's function of the time-dependent Schrödinger equation.

Let us define the function

$$S(q', q''; t) = \sum_\alpha \exp(E_\alpha t/i\hbar)\psi_\alpha(q')\psi_\alpha^*(q''), \quad (A1)$$

where $\psi_\alpha(q)$ is the normalized eigenfunction of H belonging to the eigenvalue E_α and the summation is over all eigenstates α. Then S is that solution of the differential equation

$$H'S = i\hbar\partial S/\partial t = H''S \quad (A2)$$

which satisfies the boundary condition

$$S(q', q''; 0) = \delta(q' - q''). \quad (A3)$$

Comparing these equations with (18) and (19), we see that

$$\rho_e(q', q''; \beta) = S(q', q''; -i\hbar\beta). \quad (A4)$$

Now according to the expansion theorem any Schrödinger function $\psi(q,t)$ may be written in the form

$$\psi(q,t) = \sum_\alpha c_\alpha \psi_\alpha(q) \exp(E_\alpha t/i\hbar), \quad (A5)$$

where the cs are constants. But from (A1) and the orthonormality of the ψ_αs we have

$$\psi_\alpha(q)\exp(E_\alpha t/i\hbar)=\int_{-\infty}^{+\infty} S(q,q'';t)\psi_\alpha(q'')\,dq''.$$

So (A5) may be rewritten as

$$\psi(q',t)=\int_{-\infty}^{+\infty} S(q',q'';t)\psi(q'',0)\,dq'': \qquad (A6)$$

that is, S is the Green's function of the time-dependent Schrödinger equation.

It is now possible, with the aid of (A6), to find various linear differential equations which S must satisfy. In order to do this we make use of the general theorem of quantum mechanics, that the Heisenberg matrices of the dynamic variables follow the classical equations of motion. Let such an equation for the coordinate be

$$q_t = F(p_0, q_0, t) \qquad (A7)$$

and conversely

$$q_0 = F(p_t, q_t, -t), \qquad (A8)$$

where p_t, q_t are the momentum and coordinate values at time t and p_0, q_0 are their initial values. Then the quantum mechanical matrix equation corresponding to (A7) is

$$\int_{-\infty}^{+\infty}\psi_r^*(q,t)\,q\,\psi_s(q,t)\,dq = \int_{-\infty}^{+\infty}\psi_r^*(q,0)\,F(-i\hbar\partial/\partial q, q, t)\,\psi_s(q,0)\,dq,$$

where ψ_r, ψ_s are any Schrödinger functions. On transforming $\psi_r^*(q,t)$ with the help of (A6) and $\psi_s(q,0)$ with the inverse transformation

$$\psi(q'',0) = \int_{-\infty}^{+\infty} S^*(q',q'';t)\psi(q',t)\,dq'$$

we obtain the equation

$$\iint_{-\infty}^{+\infty} \psi_r^*(q'',0)\{q' - F(-i\hbar\partial/\partial q'', q'', t)\}S^*(q',q'';t)\psi_s(q',t)\,dq'\,dq'' = 0$$

which, being valid for any ψ_r, ψ_s, implies that S^* is a solution of the eigenvalue equation

$$\{q' - F(-i\hbar\partial/\partial q'', q'', t)\}\, S^*(q',q'';t) = 0. \qquad (A9)$$

Similarly from (A8) we may derive the equation

$$\{q'' - F(-i\hbar\partial/\partial q', q', t)\}\, S(q',q'';t) = 0. \qquad (A10)$$

Now the harmonic oscillator equations of motion (A7), (A8) are of the simple linear form

$$q_t = (2\pi m\nu)^{-1} p_0 \sin 2\pi\nu t + q_0 \cos 2\pi\nu t,$$

$$q_0 = -(2\pi m\nu)^{-1} p_t \sin 2\pi\nu t + q_t \cos 2\pi\nu t.$$

The corresponding differential equations (A9), (A10) are of the first order and are readily solved to yield the expression

$$S(q',q'';t) = f(t)\exp\{-(2\pi^2 m\nu/ih)[(q'^2 + q''^2)\cot 2\pi\nu t - 2q'q''\operatorname{cosec} 2\pi\nu t]\}, \qquad (A11)$$

in which f(t) is so far unknown: it is found from (A2) to have the form

$$f(t) = C(\sin 2\pi\nu t)^{-\frac{1}{2}}, \tag{A12}$$

where C is still undetermined. Finally, the value of C is fixed by the boundary condition (A3):

$$C = (2\pi m\nu/ih)^{\frac{1}{2}}. \tag{A13}$$

Thus from (A4), (A11), (A12), (A13) we obtain for ρ_e the expression

$$\rho_e(q',q'';\beta) = \{(h/2\pi m\nu)\sinh h\nu\beta\}^{-\frac{1}{2}} \times$$

$$\exp\{-(2\pi^2 m\nu/h)[(q'^2+q''^2)\coth h\nu\beta - 2q'q''\,\mathrm{cosech}\, h\nu\beta]\}. \tag{A14}$$

APPENDIX B

Just as all the properties of an ensemble may be deduced from $\rho(q', q''; t)$, so also may they be deduced from $\rho^\dagger(p', p''; t)$, the density matrix in the momentum representation. The latter matrix is defined by the equation

$$\rho^\dagger(p',p'';t) = \sum_\alpha \rho_\alpha \phi_\alpha(p',t)\phi_\alpha^*(p'',t), \tag{B1}$$

in which the momentum function $\phi_\alpha(p,t)$ is related to the Schödinger function $\psi_\alpha(q,t)$ of equation (15) by the Fourier transformation (21). It follows from these equations that $\rho^\dagger$ is the double Fourier transform of ρ :

$$\rho^\dagger(p',p'';t) = (2\pi\hbar)^{-1}\iint_{-\infty}^{+\infty}\rho(q',q'';t)\exp\left(\frac{p'q'-p''q''}{i\hbar}\right)dq'dq''. \tag{B2}$$

The properties of the ensemble in momentum space may be derived from $\rho^\dagger$ in the same way as those in configuration space have been derived from ρ : in particular, the number density in momentum space is

$$n^\dagger(p, t) = \rho^\dagger(p, p; t). \tag{B3}$$

Let us, following Wigner (1932), define a function $f(p, q; t)$ which is the Fourier transform of both ρ and $\rho^\dagger$, that is

$$\left.\begin{aligned} f(p, q; t) &= (2\pi\hbar)^{-\frac{1}{2}}\int_{-\infty}^{+\infty}\rho(q', q''; t)\exp(ps/i\hbar)\,ds \\ &= (2\pi\hbar)^{-\frac{1}{2}}\int_{-\infty}^{+\infty}\rho^\dagger(p', p''; t)\exp(-qr/i\hbar)\,dr, \end{aligned}\right\} \tag{B4}$$

where $p = \frac{1}{2}(p' + p'')$, $q = \frac{1}{2}(q' + q'')$,

$r = p' - p''$, $s = q' - q''$.

Then the number densities n, $n^\dagger$ defined in equations (16) and (B3) may be written in terms of f as

$$n(q, t) = \int_{-\infty}^{+\infty} f(p, q; t)\,dp,$$

$$n^\dagger(p, t) = \int_{-\infty}^{+\infty} f(p, q; t)\,dq;$$

thus f has many of the properties of the classical distribution function in phase space. However, on account of the Heisenberg uncertainty principle it is not permissible to interpret f as a joint distribution function in p and q (see Green, 1952, p.232).

The function $f_e(p, q; \beta)$ describing an ensemble in

thermal equilibrium may be obtained explicitly for the harmonic oscillator from (A14) and (B4): it has the form

$$f_e(p, q; \beta) = h^{-1} \operatorname{sech}(\tfrac{1}{2}h\nu\beta) \exp\{-H(p,q)/\bar{E}\}, \quad (B5)$$

in which $\bar{E}$, the mean energy per system, is given by

$$\bar{E} = \tfrac{1}{2} h\nu \coth(\tfrac{1}{2}h\nu\beta).$$

As $h \longrightarrow 0$, the expression (B5) tends to the classical distribution function (6). One might attempt to calculate the quantum mechanical rate K merely by substituting f_e for f_c in (10), but this procedure would depend implicitly upon the incorrect "classical" interpretation of f_e.

APPENDIX C

The problem of finding the dissociation energy E_o (the least energy needed by the molecule in order to reach a configuration in which $r = r_o$) is that of finding the geometrical condition for the plane $\underline{l}\underline{q} = r_o$ to touch the quadric surface $\frac{1}{2}\tilde{\underline{q}}\,\underline{F}\,\underline{q} = E_o$. Now in general the plane $\underline{s}\underline{q} = 1$ is a tangent to the quadric $\tilde{\underline{q}}\,\underline{H}\,\underline{q} = 1$ only if its coordinates $\underline{s}$ satisfy the dual equation for the quadric, $\underline{s}\,\underline{H}^{-1}\tilde{\underline{s}} = 1$. Setting $\underline{s} = r_o^{-1}\underline{l}$, $\underline{H} = \frac{1}{2}E_o^{-1}\underline{F}$, we obtain for the dissociation energy

$$E_o = r_o^2 / 2\,\underline{l}\,\underline{F}^{-1}\tilde{\underline{l}}\,.$$

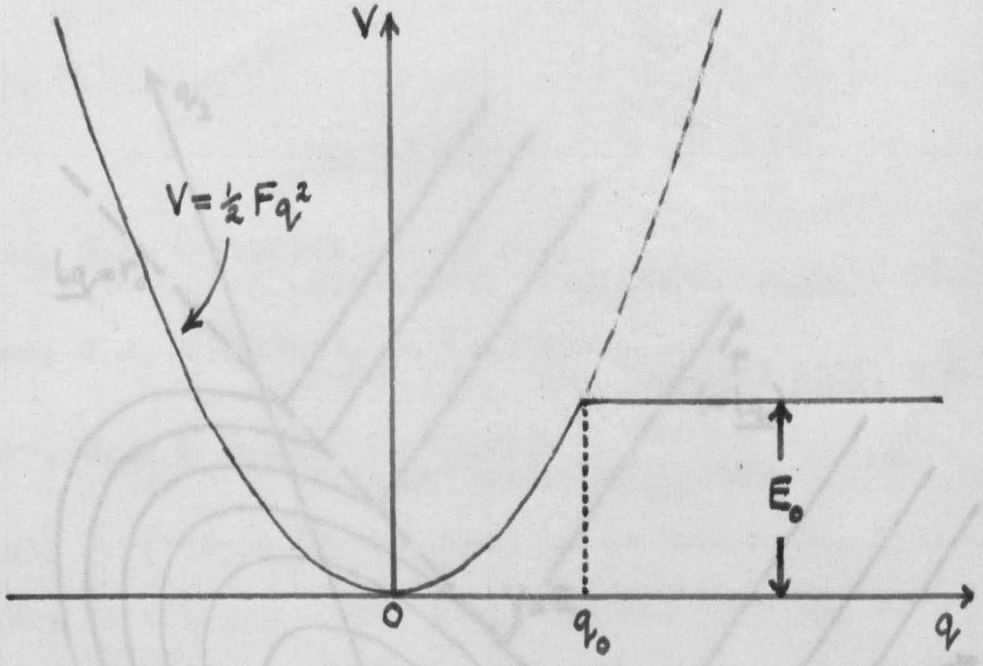

Figure 1. Potential energy of dissociating oscillator.

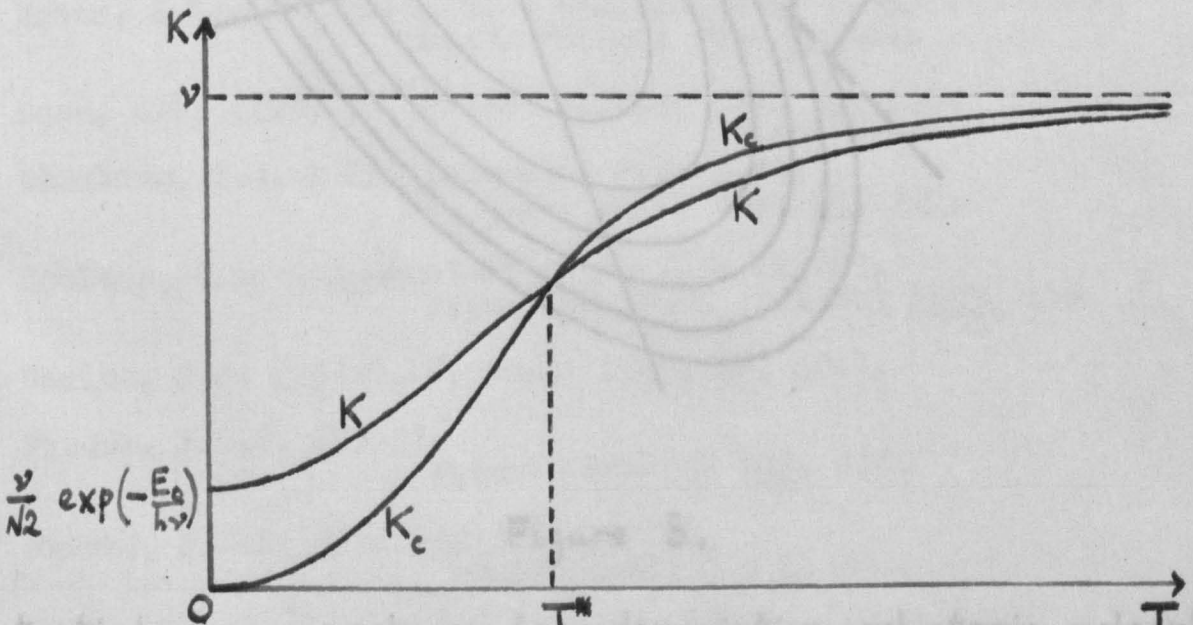

Figure 2. Quantal and classical reaction rates.

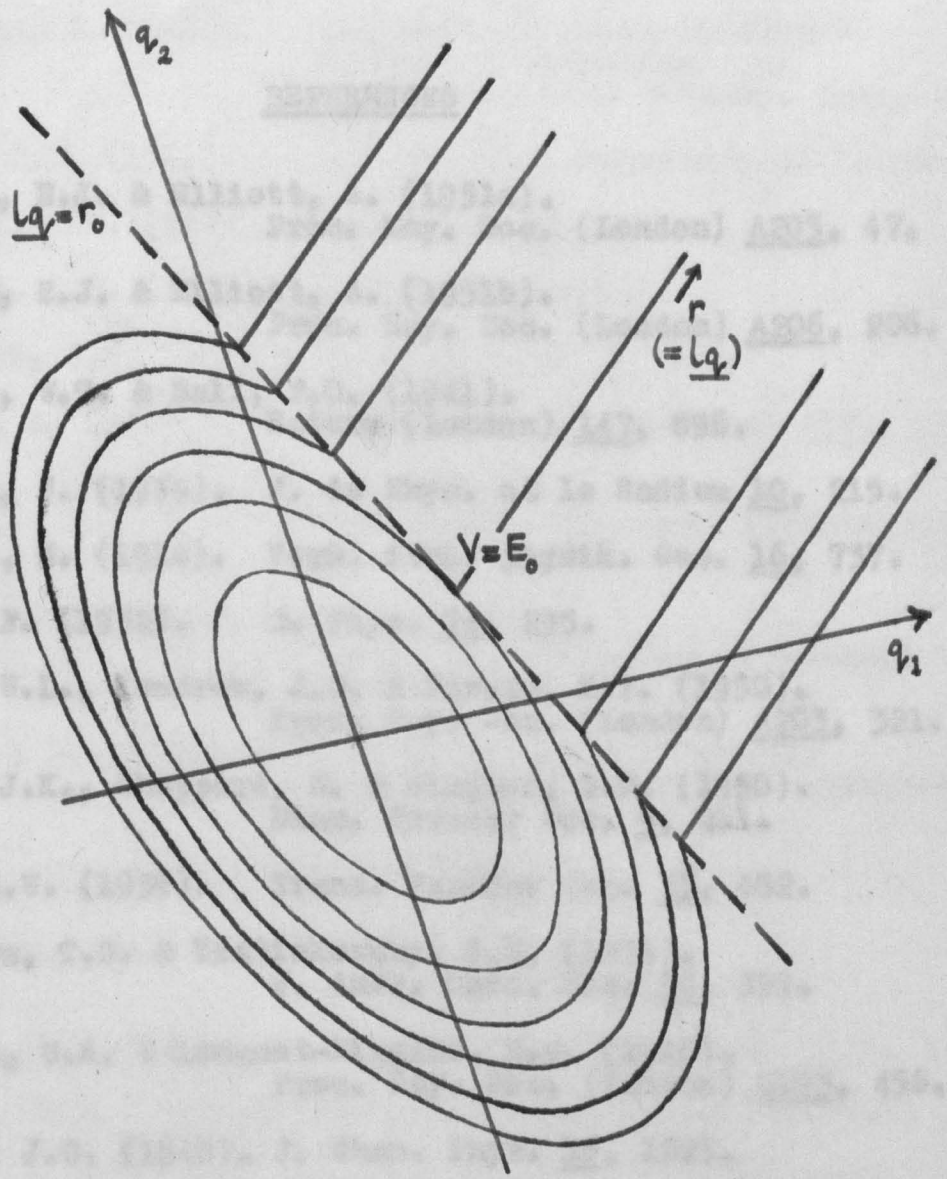

Figure 3.

Potential energy contours for dissociating polyatomic molecule.

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APPENDIX I.

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Vibrational Modifications of the Electron Distribution in Molecular Crystals. I. The Density in a Vibrating Carbon Atom

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The electron density derived from measurements of the Laue scattering of X-rays by a crystal is shown to be the density in the stationary crystal averaged over all possible displaced configurations of the atomic nuclei in thermal equilibrium together at the temperature of the experiment. The calculation of the mean electron distribution falls into two parts: in general the mean density in an atom is a function of the tensor formed by the mean square amplitudes and mean products of amplitudes of the atomic motion; for a particular crystal this tensor has to be calculated from the force constants and geometry.

In the present paper the mean density in a carbon atom is computed as a function of the r.m.s. amplitude of isotropic thermal motion. It is found that quite a small amplitude suffices to reduce the peak density considerably below the value in a stationary atom; on the other hand, the bridge density in a bond between two atoms is increased. At the amplitudes which occur in many molecular crystals at ordinary temperatures the distribution in an atom is nearly gaussian.

In Part II these results will be applied to the interpretation of some experimental distributions.

1. Introduction

Recently theoretical calculations of the electron distributions in some conjugated organic molecules have been made according to several different approximations: Klement (1951) has treated naphthalene by the valence-bond technique; March (1952) has applied both the molecular-orbital and the Thomas–Fermi methods to benzene. On the other hand, detailed electron-density contour maps derived from X-ray diffraction measurements on crystals of

naphthalene and anthracene have been published by Robertson *et al.* (Abrahams, Robertson & White, 1949*b*; Mathieson, Robertson & Sinclair, 1950). An earlier note (Coulson, Higgs & March, 1951) has pointed out the dangers of making direct comparisons between the theoretical density, calculated for a stationary molecule, and the experimental density, measured for a molecule undergoing thermal agitation in a crystal. The present papers study quantitatively the influence of thermal motion on the measured distribution.

The most striking effect of vibration on the distribution in the neighbourhood of an atom is the smearing-out of the peak which marks the position of the nucleus: the sharp strong peak in the stationary atom becomes a broad weak maximum in a vibrating atom. The height of the peak depends quite strongly on the mean amplitude of vibration, so that variations from atom to atom due to bonding in a molecule may be augmented by variations due to different atomic vibration amplitudes. The bridge values of the density between bonded atoms undergo similar modifications, but the changes are less marked than those in the peak values. Thus in general, unless allowance is first made for the effects of thermal motion, the value of a comparison between theoretical and experimental distributions is somewhat dubious.

First of all, in § 2, the motion of a vibrating polyatomic system is discussed. In § 3 it is shown that the effective density ϱ^e derived from X-ray measurements is in fact the average $\overline{\varrho}$ of ϱ for all possible configurations of the atomic nuclei forming the crystal, in thermal equilibrium together at the temperature of the experiment. In § 4 $\overline{\varrho}$ at the mean centre of a carbon atom is computed as a function of the r.m.s. amplitude of isotropic atomic vibrations, and in § 5 an estimate is made of the effect on $\overline{\varrho}$ of anisotropy. The electron distribution in carbon corresponding to a selected value of the mean amplitude is calculated in § 6 and is compared with an experimental distribution found in naphthalene; in § 7 an estimate is made of the effect on such a comparison of the termination of the Fourier series from which the experimental distribution is derived. The results are discussed in § 8.

The results will be applied to the interpretation of the observed peaks in naphthalene, anthracene and other molecules in Part II.

2. Harmonic vibrations of a polyatomic system

Let us first consider the motion of a crystal as a system of N atoms vibrating about an equilibrium configuration. Let the instantaneous displacement of the rth atomic nucleus, of mass m_r, have cartesian components (x_r, y_r, z_r). Then in matrix notation, the order of the coordinates being

$$(x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N) ,$$

the kinetic energy of the system is

$$T = \tfrac{1}{2}\dot{\mathbf{x}}'\mathbf{M}\dot{\mathbf{x}} , \tag{1}$$

where

$$\mathbf{M} = \text{diag}\,(m_1, m_1, m_1, m_2, m_2, m_2, \ldots, m_N, m_N, m_N) .$$

The potential energy is, to a first approximation,

$$V = \tfrac{1}{2}\mathbf{x}'\mathbf{F}\mathbf{x} , \tag{2}$$

where $\mathbf{F}$ is the matrix of force constants. From the symmetric matrices, $\mathbf{M}$ and $\mathbf{F}$, another may be constructed, namely the dynamical matrix (Born, 1942),

$$\mathbf{D} = \mathbf{M}^{-\frac{1}{2}}\mathbf{F}\mathbf{M}^{-\frac{1}{2}} . \tag{3}$$

The vibration frequencies ν of the system are then the $3N$ solutions of the secular equation,

$$|\mathbf{D}-\omega^2\mathbf{I}| = 0 ,$$

in which $\mathbf{I}$ is the unit matrix and $\omega = 2\pi\nu$. Normal coordinates $\mathbf{q}$ are obtained from $\mathbf{x}$ by the transformation,

$$\mathbf{x} = \mathbf{M}^{-\frac{1}{2}}\mathbf{U}\mathbf{q} . \tag{4}$$

The ith column of $\mathbf{U}$ consists of the normalized amplitudes of $\mathbf{x}$ in the ith normal mode of vibration, that is, $\mathbf{U}$ is an orthogonal matrix ($\mathbf{U}'\mathbf{U}=\mathbf{I}=\mathbf{U}\mathbf{U}'$) which satisfies the equation,

$$\mathbf{D}\mathbf{U} = \mathbf{U}\boldsymbol{\Lambda} ,$$

where $\boldsymbol{\Lambda} = \text{diag}\,(\omega_i^2)$. It follows from the last equation that

$$\mathbf{D}^n = \mathbf{U}\boldsymbol{\Lambda}^n\mathbf{U}' ,$$

where n is any integer, positive or negative, and more generally that

$$f(\mathbf{D}) = \mathbf{U}f(\boldsymbol{\Lambda})\mathbf{U}' , \tag{5}$$

where $f(z)$ is any regular function of z.

Expressed in terms of normal coordinates, the hamiltonian of the system is

$$H = T+V = \tfrac{1}{2}\sum_{i=1}^{3N}(\dot{q}_i^2+\omega_i^2 q_i^2) .$$

Now Bloch (1932) has shown, for a harmonic oscillator of hamiltonian $\frac{1}{2}(\dot{q}^2+\omega^2q^2)$ in thermal equilibrium with its environment at temperature T, that the probability that q lies in the range $(q, q+dq)$ is

$$P(q)dq = (\gamma/2\pi)^{\frac{1}{2}}\exp(-\tfrac{1}{2}\gamma q^2)dq , \tag{6}$$

in which

$$\gamma^{-1} = \overline{q^2} = (\hbar/2\omega)\coth(\hbar\omega/2kT) ,$$

where k is Boltzmann's constant and $\hbar$ is Planck's constant divided by 2π. Since the normal coordinates are dynamically independent (in the sense that $H(\mathbf{q}) = \sum_i H_i(q_i)$, so that any total eigenfunction has the form $\psi(\mathbf{q}) = \prod_i \psi_i(q_i)$), the probability that all the q_i lie in the corresponding ranges (q_i, q_i+dq_i) equals

the product of the probabilities of the individual situations:

$$P(\mathbf{q})\,d\mathbf{q} = \prod_i P_i(q_i)\,dq_i$$
$$= \{|\mathbf{\Gamma}|/(2\pi)^{3N}\}^{\frac{1}{2}} \exp\,(-\tfrac{1}{2}\mathbf{q}'\mathbf{\Gamma}\mathbf{q})\,d\mathbf{q}\,,$$

in which

$$d\mathbf{q} = \prod_{i=1}^{3N} dq_i$$

and

$$\mathbf{\Gamma}^{-1} = \overline{\mathbf{q}\mathbf{q}'} = \varphi(\mathbf{\Lambda})\,,$$

where

$$\varphi(z) = \tfrac{1}{2}\hbar z^{-\frac{1}{2}} \coth\,(\hbar z^{\frac{1}{2}}/2kT)\,.$$

Transforming to the coordinates $\mathbf{x}$ according to equation (4) and using the consequent relation $d\mathbf{x} = |\mathbf{M}^{-\frac{1}{2}}\mathbf{U}|\,d\mathbf{q}$, we find that the probability that $\mathbf{x}$ lies in the range $(\mathbf{x}, \mathbf{x}+\mathbf{dx})$ is

$$P(\mathbf{x})d\mathbf{x} = P(\mathbf{q})\,d\mathbf{q}$$
$$= \{|\mathbf{A}|/(2\pi)^{3N}\}^{\frac{1}{2}} \exp\,(-\tfrac{1}{2}\mathbf{x}'\mathbf{A}\mathbf{x})\,d\mathbf{x}\,, \qquad (7)$$

in which

$$\mathbf{A}^{-1} = \mathbf{M}^{-\frac{1}{2}}\mathbf{U}\mathbf{\Gamma}^{-1}\mathbf{U}'\mathbf{M}^{-\frac{1}{2}}$$
$$= \overline{\mathbf{x}\mathbf{x}'}$$
$$= \mathbf{M}^{-\frac{1}{2}}\varphi(\mathbf{D})\mathbf{M}^{-\frac{1}{2}}\,, \qquad (8)$$

by equation (5). More generally it follows from (6) that the probability distribution for any subset $\mathbf{x}_1$ of the coordinates $\mathbf{x}$, irrespective of the values of the remaining coordinates, has the gaussian form,

$$P(\mathbf{x}_1)d\mathbf{x}_1 = \{|\mathbf{A}_1|/(2\pi)^n\}^{\frac{1}{2}} \exp\,(-\tfrac{1}{2}\mathbf{x}_1'\mathbf{A}_1\mathbf{x}_1)d\mathbf{x}_1\,, \quad (7a)$$

where

$$\mathbf{A}_1^{-1} = \overline{\mathbf{x}_1\mathbf{x}_1'} \qquad (8a)$$

and n is the dimension of $\mathbf{x}_1$.

3. Effects of thermal motion on the scattering of X-rays by crystals

The influence of thermal motion on X-ray scattering has been discussed fully by Born & Sarginson (1941); some of their conclusions will be quoted here. Broadly, two effects may be distinguished: first, the Laue spots are weakened by the smearing-out of the electron density; secondly, there is a diffuse background intensity due to the relaxation of strict periodicity in the crystal lattice. We are concerned here with the former effect.

The modified Laue scattering is derived from that for a rigid crystal by changing the scattering factor for the jth atom in the unit cell from the value f_j for a stationary atom to the value

$$g_j = f_j \exp\,(-L_j) \qquad (9)$$

for a vibrating one. The simplest formula for L_j is that given by Born (1943):

$$L_j = \frac{2\pi^2}{m_j} \sum_{x,y} S_{u,\,jj,\,xy} k_x k_y\,, \qquad (10)$$

where $\mathbf{k} = (\mathbf{k}_s - \mathbf{k}_i)$ is the difference between the wave-vectors of the scattered and incident radiation ($|\mathbf{k}_s| = |\mathbf{k}_i| = \lambda^{-1}$, where λ is the wavelength) and $\mathbf{S} = \varphi(\mathbf{D})$ is the scattering matrix (Born, 1942) for the crystal (the suffix l numbers the unit cells). Combining (8) and (10) we obtain the relation,

$$L_j = 2\pi^2 \sum_{x,\,y} \overline{x_j y_j} k_x k_y$$
$$= 2\pi^2 \mathbf{k}'\,\overline{\mathbf{u}_j\mathbf{u}_j'}\,\mathbf{k}\,, \qquad (11)$$

in which $\mathbf{u}_j$ is the column vector with components (x_j, y_j, z_j). Alternatively, equation (11) may be written as

$$L_j = \frac{8\pi^2 \sin^2\theta}{\lambda^2}\,\overline{u_{j,\,\mathbf{k}}^2}\,, \qquad (11a)$$

where θ is the Bragg angle and $u_{j,\,\mathbf{k}}$ is the component of the displacement of the jth atom parallel to $\mathbf{k}$ (*i.e.* normal to the reflecting plane).

Let us now consider the electron distribution in atom j. The density in a stationary atom is the Fourier transform of f : at a point $\mathbf{r}_j$ from the nucleus it is

$$\varrho_j(\mathbf{r}_j) = \int f_j(\mathbf{k}) \exp\,(2\pi i\,\mathbf{k}'\mathbf{r}_j)\,d\mathbf{k}\,; \qquad (12)$$

conversely

$$f_j(\mathbf{k}) = \int \varrho_j(\mathbf{r}_j) \exp\,(-2\pi i\mathbf{k}'\mathbf{r}_j)d\mathbf{r}_j\,. \qquad (12a)$$

The effective density derived from the actual Laue intensities is similarly

$$\varrho_j^e(\mathbf{r}_j) = \int g_j(\mathbf{k}) \exp\,(2\pi i\mathbf{k}'\mathbf{r}_j)d\mathbf{k}\,. \qquad (13)$$

From (9), (11), (13) and (12a) we find

$$\varrho_j^e(\mathbf{r}_j)$$
$$= \iint \varrho_j(\mathbf{t}_j) \exp\,[-2\pi^2\mathbf{k}'\overline{\mathbf{u}_j\mathbf{u}_j'}\,\mathbf{k} + 2\pi i\,\mathbf{k}'(\mathbf{r}_j - \mathbf{t}_j)]\,d\mathbf{k}\,d\mathbf{t}$$
$$= \int \varrho_j(\mathbf{t}_j) Q(\mathbf{r}_j - \mathbf{t}_j)\,d\mathbf{t}_j$$
$$= \int \varrho_j(\mathbf{r}_j - \mathbf{u}_j) Q(\mathbf{u}_j)\,d\mathbf{u}\,, \qquad (14)$$

in which

$$Q(\mathbf{u}_j) = \int \exp\,(-2\pi^2\mathbf{k}'\mathbf{A}_j^{-1}\mathbf{k} + 2\pi i\mathbf{k}'\mathbf{u}_j)\,d\mathbf{k}$$
$$= \exp\,(-\tfrac{1}{2}\mathbf{u}_j'\mathbf{A}_j\mathbf{u}_j) \int \exp\,(-2\pi^2\mathbf{k}_1'\mathbf{A}_j\mathbf{k}_1)\,d\mathbf{k}\,,$$

where

$$\mathbf{A}_j^{-1} = \overline{\mathbf{u}_j\mathbf{u}_j'} \qquad (15)$$

and

$$\mathbf{k}_1 = \mathbf{k} + (2\pi i)^{-1}\mathbf{A}_j\mathbf{u}_j\,.$$

Now

$$\int \exp\,(-2\pi^2\mathbf{k}_1'\mathbf{A}_j^{-1}\mathbf{k}_1)\,d\mathbf{k} = \{|\mathbf{A}_j|/(2\pi)^3\}^{\frac{1}{2}}\,,$$

so that

$$Q(\mathbf{u}_j) = \{|\mathbf{A}_j|/(2\pi)^3\}^{\frac{1}{2}} \exp\,(-\tfrac{1}{2}\mathbf{u}_j'\mathbf{A}_j\mathbf{u}_j)$$
$$= P(\mathbf{u}_j)\,, \qquad (16)$$

as is evident from (7a) and (8a) with $\mathbf{x}_1 = \mathbf{u}_j$, and the definition (15). Combining (14) and (16) we find that

$$\varrho_j^e(\mathbf{r}_j) = \int \varrho_j(\mathbf{r}_j - \mathbf{u}_j) P(\mathbf{u}_j)\, d\mathbf{u}_j = \overline{\varrho}_j(\mathbf{r}_j)\,, \tag{17}$$

the thermal average of the density. Thus the distribution which is derived from X-ray diffraction measurements is

$$\overline{\varrho}(\mathbf{r}) = \{|\mathbf{A}|/(2\pi)^3\}^{\frac{1}{2}} \int \varrho(\mathbf{r}-\mathbf{u}) \exp(-\tfrac{1}{2}\mathbf{u}'\mathbf{A}\mathbf{u})\, d\mathbf{u}\,, \tag{18}$$

where $\mathbf{A}^{-1} = \overline{\mathbf{u}\mathbf{u}'}$ and the suffix j has been dropped.

4. Calculation of $\overline{\varrho}$ for carbon

The calculation of $\overline{\varrho}$ for a given atom such as carbon falls into two distinct parts. In general $\overline{\varrho}$ is to be found as a function of $\mathbf{r}$ and $\mathbf{A}$; in particular problems $\mathbf{A}$ has to be derived from the geometry and force constants of the crystal by means of equation (8). At present we are concerned with the former problem; an example of the latter will be considered in Part II.

It is necessary to make certain assumptions about ϱ, the stationary density. Already, by using atomic scattering factors f_j in the theory, we have implicitly neglected bonding. As is customary in X-ray scattering theory, we shall derive ϱ from the Hartree self-consistent field for free carbon. The field will be taken as that for the spherically symmetric valence state, $(1s)^2(2s)(2p_x)(2p_y)(2p_z)$, which predominates in bonded carbon: in terms of the radial distribution functions, R, S and T, computed by Torrance (1934) $\varrho(\mathbf{r})$ is given by

$$\varrho(\mathbf{r}) = (4\pi r^2)^{-1}(2R^2+S^2+3T^2)\,. \tag{19}$$

When ϱ is a spherically symmetric function such as (19), it is convenient to use a coordinate system whose axes lie along the principal axes of $\mathbf{A}$: the probability distribution then assumes the simpler form,

$$P(\mathbf{u})d\mathbf{u} = \{abc/(2\pi)^3\}^{\frac{1}{2}} \exp[-\tfrac{1}{2}(a\xi^2+b\eta^2+c\zeta^2)]d\mathbf{u}\,, \tag{20}$$

in which (ξ, η, ζ) are the components of $\mathbf{u}$,

$$d\mathbf{u} = d\xi\, d\eta\, d\zeta\,,$$

and

$$a^{-1} = \overline{\xi^2},\ b^{-1} = \overline{\eta^2},\ c^{-1} = \overline{\zeta^2}\,.$$

Thus $\overline{\varrho}(\mathbf{r})$ may be expressed as a function of (x, y, z), the components of $\mathbf{r}$ along the principal axes of $\mathbf{A}$, and of (a, b, c), the principal values of $\mathbf{A}$.

Inspection of (18) shows that when $\varrho(\mathbf{r})$ is an even function, so also is $\overline{\varrho}(\mathbf{r})$: it therefore has a symmetrical maximum at $\mathbf{r} = 0$, the mean centre of the atom. The value of this peak density is, according to (18), (19) and (20),

$$\overline{\varrho}(0) = \{abc/(2\pi)^3\}^{\frac{1}{2}} \iiint_{-\infty}^{+\infty} (4\pi u^2)^{-1}[2R^2(u)+S^2(u)+3T^2(u)] \times \exp[-\tfrac{1}{2}(a\xi^2+b\eta^2+c\zeta^2)]\, d\xi\, d\eta\, d\zeta\,,$$

in which u is the radial atomic displacement ($u^2 = \xi^2+\eta^2+\zeta^2$). On transformation to spherical polar coordinates this integral becomes

$$\overline{\varrho}(0) = \int_0^\infty (2R^2+S^2+3T^2)F(u)\, du\,, \tag{21}$$

in which

$$F(u) = (4\pi)^{-1}\{abc/(2\pi)^3\}^{\frac{1}{2}} \int_0^{2\pi}\left\{\int_0^{\pi} \exp[-\tfrac{1}{2}u^2(\alpha+\beta\cos^2\theta)] \times \sin\theta\, d\theta\right\} d\varphi\,,$$

where

$$\alpha(\varphi) = a\cos^2\varphi + b\sin^2\varphi$$

and

$$\beta(\varphi) = c-\alpha(\varphi)\,. \tag{22}$$

The integration with respect to θ may be carried out and yields the formula,

$$F(u) = (abc)^{\frac{1}{2}}(8\pi^2 u)^{-1} \int_0^{2\pi} \exp(-\tfrac{1}{2}u^2\alpha)\beta^{-\frac{1}{2}} H(u\sqrt{\tfrac{1}{2}\beta})\, d\varphi\,, \tag{23}$$

where H is the error function defined by

$$H(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-t^2)\, dt\,.$$

In the present section we shall consider only the simplest case of (23), that which occurs when the vibration is isotropic. When $\overline{\xi^2} = \overline{\eta^2} = \overline{\zeta^2} = \tfrac{1}{3}\overline{u^2}$, then also $a = b = c = 3(\overline{u^2})^{-1}$, so that $\mathbf{A} = a\mathbf{I}$. It follows that $\alpha = a$, $\beta = 0$, and (23) may be integrated to give

$$F(u) = (a/2\pi)^{\frac{3}{2}} \exp(-\tfrac{1}{2}au^2)\,. \tag{24}$$

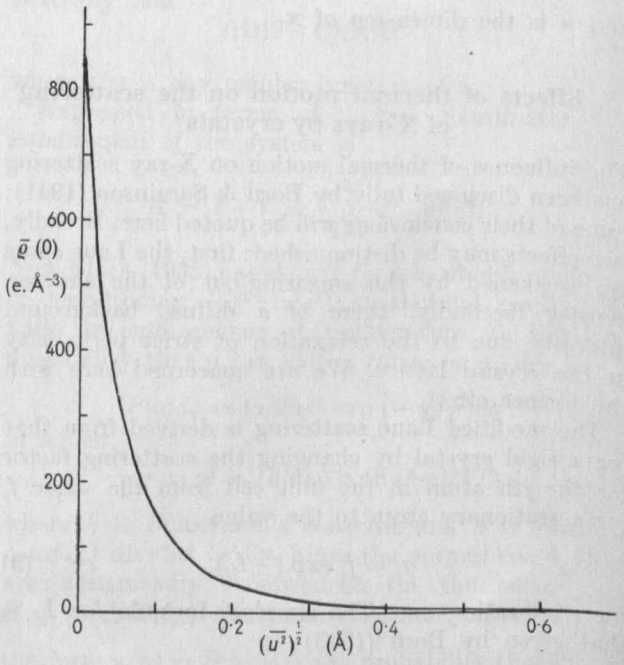

Fig. 1. Peak density in carbon as a function of thermal amplitude.

Table 1. *Peak density in carbon for various r.m.s. displacements*

$(\overline{u^2})^{\frac{1}{2}}$ (Å)	$\bar{\varrho}_{1s}(0)$ (e.Å^{-3})	$\bar{\varrho}_{2s}(0)$ (e.Å^{-3})	$\bar{\varrho}_{2p}(0)$ (e.Å^{-3})	$\bar{\varrho}(0)$ (e.Å^{-3})	v (%)
0	413·3	20·4	0	847	2·4
0·008	352·4	17·3	0·00	722	2·4
0·016	298·5	14·6	0·01	612	2·4
0·023	262·2	12·8	0·02	537	2·4
0·032	219·6	10·7	0·04	450	2·4
0·046	172·9	8·3	0·07	354	2·4
0·065	125·9	5·9	0·11	258	2·4
0·084	93·79	4·23	0·15	192	2·4
0·091	83·38	3·70	0·16	171	2·4
0·102	71·35	3·10	0·18	146	2·5
0·129	49·43	2·03	0·23	102	2·7
0·155	35·96	1·40	0·26	74·1	2·9
0·205	20·70	0·77	0·30	43·1	3·9
0·264	11·70	0·47	0·33	24·8	5·8
0·373	4·972	0·316	0·314	11·2 (11·2)	11·2
0·457	2·908	0·281	0·286	6·95 (6·95)	16·4
0·647	1·114	0·223	0·213	3·09 (3·10)	27·9

Table 2. *Analytical approximation to* $\bar{\varrho}(0)$.

$(\overline{u^2})^{\frac{1}{2}}$ (Å)	$\bar{\varrho}(0)$ (e.Å^{-3})	$(\overline{u^2})^{\frac{1}{2}}$ (Å)	$\bar{\varrho}(0)$ (e.Å^{-3})	$(\overline{u^2})^{\frac{1}{2}}$ (Å)	$\bar{\varrho}(0)$ (e.Å^{-3})
0·30	18·5	0·42	8·45	0·54	4·72
0·31	17·1	0·43	8·00	0·55	4·52
0·32	15·9	0·44	7·59	0·56	4·34
0·33	14·8	0·45	7·20	0·57	4·16
0·34	13·8	0·46	6·85	0·58	4·00
0·35	12·9	0·47	6·51	0·59	3·84
0·36	12·1	0·48	6·20	0·60	3·70
0·37	11·4	0·49	5·91	0·61	3·56
0·38	10·7	0·50	5·64	0·62	3·43
0·39	10·0	0·51	5·39	0·63	3·30
0·40	9·47	0·52	5·15	0·64	3·18
0·41	8·94	0·53	4·93	0·65	3·07

$\bar{\varrho}(0)$ was computed for a series of values of a by using (21) and (24): it is tabulated in Table 1, and in Fig. 1 it is plotted against $(\overline{u^2})^{\frac{1}{2}}$, the r.m.s. amplitude of vibration ($\overline{u^2} = 3a^{-1}$). The other quantities in Table 1 are $\bar{\varrho}_{1s}(0)$, $\bar{\varrho}_{2s}(0)$ and $\bar{\varrho}_{2p}(0)$, the contributions to $\bar{\varrho}(0)$ per $1s$, $2s$ and $2p$ electron respectively, and $v(0)$, the percentage contribution from all the valence electrons ($\bar{\varrho} = 2\bar{\varrho}_{1s} + \bar{\varrho}_{2s} + 3\bar{\varrho}_{2p}$; $v = (100/\bar{\varrho})[\varrho_{2s} + 3\bar{\varrho}_{2p}]$). A graph of v against $(\overline{u^2})^{\frac{1}{2}}$ is plotted in Fig. 2. When a is small, i.e. when $(\overline{u^2})^{\frac{1}{2}}$ is large,

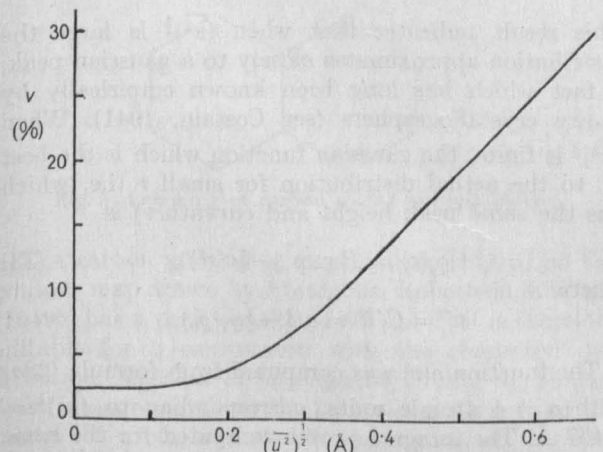

Fig. 2. Percentage valence-electron contribution to $\bar{\varrho}(0)$ as a function of thermal amplitude.

$$F(u) \simeq (a/2\pi)^{\frac{3}{2}},$$

provided that u is not too large. Since R, S and T fall off rapidly at large distances from the nucleus, it follows from (21) that the asymptotic form of $\bar{\varrho}(0)$ for large $(\overline{u^2})^{\frac{1}{2}}$ is

$$\bar{\varrho}(0) \simeq (a/2\pi)^{\frac{3}{2}} \int_0^\infty (2R^2 + S^2 + 3T^2)\, du$$

$$= 6(2\pi\overline{u^2}/3)^{-\frac{3}{2}}, \qquad (25)$$

since R, S and T are normalized to unity. This result suggests that it may be possible to approximate to $\bar{\varrho}(0)$ over a moderate range of values of $(\overline{u^2})^{\frac{1}{2}}$ by a function of the form $C(\overline{u^2})^{-n}$. In fact it was found that the curve of Fig. 1 is fitted closely over the range $(\overline{u^2})^{\frac{1}{2}} = 0{\cdot}30$–$0{\cdot}65$ Å ($\bar{\varrho}(0) = 18$–3 e.A^{-3}) by the formula

$$\bar{\varrho}(0) \simeq 1{\cdot}13(\overline{u^2})^{-1{\cdot}16}; \qquad (26)$$

this function is tabulated in Table 2. The numbers in brackets in Table 1, column 5 are approximate values of $\bar{\varrho}(0)$ calculated from (26): comparison with the directly computed values indicates that (26) yields values which are accurate to less than 1% in the range covered by Table 2.

5. Effect ofanisotropy

An estimate of the effect on $\bar{\varrho}(0)$ of anisotropy in the atomic motion may be made by considering the special case of anisotropy in one direction only. If $b = a$ and $c = a(1+\Delta)$, where Δ is an anisotropy parameter, then in (22) $\alpha(\varphi) = a$ and $\beta(\varphi) = a\Delta$, so that (23) may be integrated to give

$$F(u) = \left(\frac{1+\Delta}{\Delta}\right)^{\frac{1}{2}} \frac{a}{4\pi u} \exp(-\tfrac{1}{2}au^2) H(u\sqrt{\tfrac{1}{2}a\Delta}) . \quad (27)$$

The r.m.s. amplitude is then

$$(\overline{u^2})^{\frac{1}{2}} = \left[\frac{3+2\Delta}{a(1+\Delta)}\right]^{\frac{1}{2}} .$$

$\bar{\varrho}(0)$ was calculated from (21) and (27) for the special values, $a = 4$ atomic units, $\Delta = \frac{1}{2}$: these correspond to $(\overline{u^2})^{\frac{1}{2}} = 0{\cdot}431$ Å, $(\overline{\zeta^2}/\overline{\xi^2})^{\frac{1}{2}} = 0{\cdot}82$. The value found was 8·13 e.Å^{-3}, which differs by less than 2% from the value 8·00 e.Å^{-3} for isotropic motion. It appears that a considerable degree of anisotropy would be required to produce a serious change in $\bar{\varrho}(0)$. Conversely, $\bar{\varrho}(0) = 8{\cdot}13$ e.Å^{-3} corresponds to an isotropic r.m.s. amplitude of 0·427 Å (Table 2), which differs by 1% from the anisotropic value, 0·431 Å. Thus, for such a degree of anisotropy, the error in $(\overline{u^2})^{\frac{1}{2}}$, calculated from $\bar{\varrho}(0)$ on the assumption of isotropy, is quite small.

6. Isotropic motion: the electron distribution

When the atomic motion is isotropic ($\mathbf{A} = a\mathbf{I}$) and the stationary distribution has spherical symmetry, equation (18) becomes

$$\bar{\varrho}(\mathbf{r}) = (a/2\pi)^{\frac{3}{2}} \int \varrho(t) \exp(-\tfrac{1}{2}au^2) d\mathbf{t} ,$$

in which $\mathbf{t} = \mathbf{r} - \mathbf{u}$ (see Fig. 3). On transforming to spherical polar coordinates in $\mathbf{t}$-space with the polar axis along $\mathbf{r}$, and using the relation,

$$u^2 = r^2 + t^2 - 2rt\cos\theta ,$$

we obtain

$$\bar{\varrho}(\mathbf{r}) = (a/2\pi)^{\frac{3}{2}} \exp(-\tfrac{1}{2}ar^2) \int_0^\infty \varrho(t) \exp(-\tfrac{1}{2}at^2) \times \left\{\int_0^\pi \exp(art\cos\theta) \sin\theta d\theta\right\} t^2 dt \int_0^{2\pi} d\varphi .$$

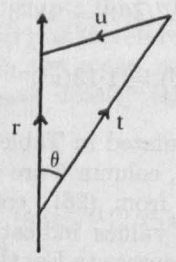

Fig. 3. Coordinates used in integration of $\bar{\varrho}(r)$.

On carrying out the θ and φ integrations, we find that $\bar{\varrho}$ has the spherically symmetric form,

$$\bar{\varrho}(r) = 4\pi(a/2\pi)^{\frac{3}{2}} \exp(-\tfrac{1}{2}ar^2) \int_0^\infty \varrho(t) \exp(-\tfrac{1}{2}at^2) \times \frac{\sinh(art)}{(art)} t^2 dt . \quad (28)$$

In terms of the radial distribution function,

$$D(r) = 4\pi r^2 \varrho(r) = 2R^2 + S^2 + 3T^2 ,$$

this may be written as

$$\bar{\varrho}(r) = (a/2\pi)^{\frac{3}{2}} \exp(-\tfrac{1}{2}ar^2) \int_0^\infty D(t) \exp(-\tfrac{1}{2}at^2) \times \frac{\sinh(art)}{(art)} dt . \quad (28a)$$

By expanding the function $(art)^{-1}\sinh(art)$ as a power series we obtain a formal series expansion of $\bar{\varrho}(r)$:

$$\bar{\varrho}(r) = \exp(-\tfrac{1}{2}ar^2) \sum_{n=0}^{\infty} \frac{\varrho_n(a)}{(2n+1)!} (ar^2)^n , \quad (28b)$$

where

$$\varrho_n(a) = (a/2\pi)^{\frac{3}{2}} \int_0^\infty (at^2)^n D(t) \exp(-\tfrac{1}{2}at^2) dt . \quad (29)$$

From (28b) we derive formulae for the height of the density peak and its curvature:

$$P(a) \equiv \bar{\varrho}(0) = \varrho_0 , \quad (30)$$

the function computed in § 4;

$$C(a) \equiv -\left(\frac{d^2\bar{\varrho}}{dr^2}\right)_{r=0} = a(\varrho_0 - \tfrac{1}{3}\varrho_1) . \quad (31)$$

The asymptotic form of $\bar{\varrho}(r)$ for large r.m.s. amplitudes may be obtained from (28a) by allowing a to tend to zero: the integral tends to the value $\int_0^\infty D(t)dt = 6$, so the asymptotic form of the distribution is

$$\bar{\varrho}(r) \cong 6(a/2\pi)^{\frac{3}{2}} \exp(-\tfrac{1}{2}ar^2) . \quad (32)$$

This result indicates that when $(\overline{u^2})^{\frac{1}{2}}$ is large the distribution approximates closely to a gaussian peak, a fact which has long been known empirically by X-ray crystallographers (see Costain, 1941). When $(\overline{u^2})^{\frac{1}{2}}$ is finite, the gaussian function which is the best fit to the actual distribution for small r (i.e. which has the same peak height and curvature) is

$$\bar{\varrho}_g(r) = P \exp(-\tfrac{1}{2}a'r^2) , \quad (33)$$

where

$$a' = C/P = a(1 - \tfrac{1}{3}\varrho_1/\varrho_0) .$$

The function $\bar{\varrho}(r)$ was computed from formula (28a) with $a = 4$ atomic units, corresponding to $(\overline{u^2})^{\frac{1}{2}} = 0{\cdot}457$ Å. The integral ϱ_1 was computed for the same value of a, and from it and ϱ_0 (Table 1, column 5) the parameters in the gaussian function $\bar{\varrho}_g$ were found:

$P = 6{\cdot}955$ e.Å^{-3},
$a' = 11{\cdot}24$ Å^{-2},
$C = a'P = 78{\cdot}16$ e.Å^{-5}.

Both functions are tabulated in Table 3 and displayed

Table 3. *Electron distribution in carbon*

$(\overline{u^2})^{\frac{1}{2}} = 0{\cdot}457$ Å

r (Å)	$\bar{\varrho}$ (e.Å^{-3})	$\bar{\varrho}_g$ (e.Å^{-3})
0	6·955	6·955
0·132	6·309	6·306
0·264	4·744	4·700
0·396	3·030	2·880
0·528	1·730	1·450
0·660	0·956	0·600

graphically in Fig. 4: it is seen that $\bar{\varrho}(r)$ is closely gaussian up to about 0·4 Å from the centre.

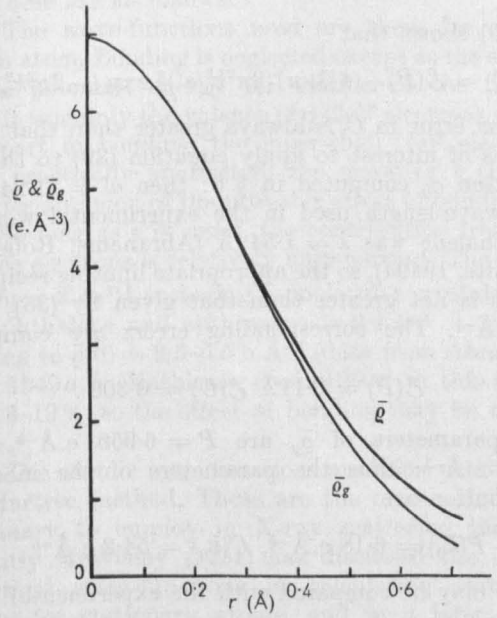

Fig. 4. Electron distribution $\bar{\varrho}(r)$ for carbon at $(\overline{u^2})^{\frac{1}{2}} = 0{\cdot}457$ Å, and gaussian curve $\bar{\varrho}_g(r)$.

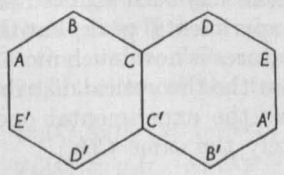

Fig. 5. Labelling of carbon atoms in naphthalene.

The carbon atom A in naphthalene (Fig. 5) on the contour map drawn by Abrahams, Robertson & White (1949*b*) has a peak density of 6·9 e.Å^{-3}; it is therefore suitable for a comparison with the computed distribution. A graph of $\ln \bar{\varrho}$ against r^2 (Fig. 6), plotted from measurements on the map along a line from the centre of atom A towards the centre of the ring (to reduce the effect of overlap from neighbouring atoms), is roughly linear up to $r = 0{\cdot}6$ Å: thus the experimental distribution is closely gaussian. However, the curvature of the experimental peak is 57 e.Å^{-5}, considerably less than the calculated 78 e.Å^{-5}. The

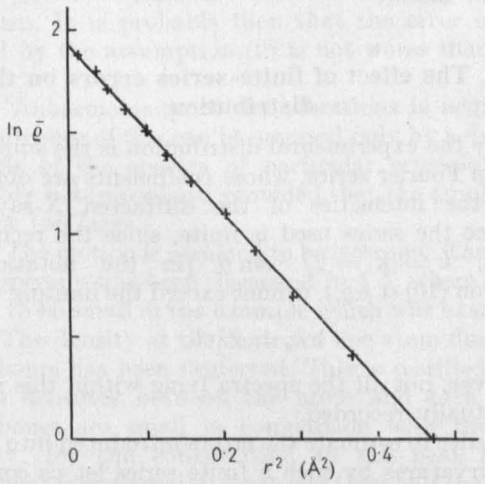

Fig. 6. Plot of $\ln \bar{\varrho}$ *v.* r^2 for atom A of naphthalene (from measurements on Robertson's map).

source of this discrepancy probably lies in the use of a finite Fourier series in the calculation of the experimental distribution: this point is discussed more fully below in § 7.

The foregoing calculations permit us to estimate the effect of thermal motion on the bridge value of the density in a bond between two carbon atoms. If the change in the distribution due to bonding is neglected and the r.m.s. amplitudes of the two atoms are assumed to be equal, the bridge density is

$$B(a) = 2\bar{\varrho}(\tfrac{1}{2}l)\,, \qquad (34)$$

where l is the bond-length. Taking $l = 1{\cdot}4$ Å (a value typical of bonds belonging to benzene rings) and $(\overline{u^2})^{\frac{1}{2}} = 0{\cdot}457$ Å (corresponding to the peak, $P = 6{\cdot}9$ e.Å^{-3}, in atom A of naphthalene), we find $B = 1{\cdot}60$ e.Å^{-3} by extrapolating the data of Table 3 to $r = 0{\cdot}7$ Å. This value may be compared with $B = 1{\cdot}27$ e.Å^{-3}, computed directly from the Hartree field for stationary atoms. The motion increases B by 0·33 e.Å^{-3}.

An estimate of the accuracy of the approximate equation (34) may be made by considering the electron distribution in benzene calculated by March (1952). For the bridge density in a stationary C–C bond according to the molecular-orbital theory March gives the value 1·9 e.Å^{-3}. A calculation using the same analytical wave-functions (Slater, 1930) and the 'overlapping atom' approximation (34) yields the value 1·58 e.Å^{-3} for the same density. The difference, about 0·3 e.Å^{-3}, represents the effect of bonding: it is roughly equal to the increase in the Hartree-field density due to thermal motion. Clearly an adequate treatment of bridge densities must take both effects into account.

It may be remarked that the bridge values without,

bonding or vibration, calculated from Hartree and Slater atomic wave-functions also differ by 0·3 e.Å^{-3}. Thus the choice of wave-functions is another important factor.

7. The effect of finite-series errors on the distribution

Ideally the experimental distribution is the sum of an infinite Fourier series, whose coefficients are obtained from the intensities of the diffracted X-rays. In practice the series used is finite, since the reciprocal radius, $k = |\mathbf{k}| = 2\lambda^{-1}\sin\theta$ (in the notation of equation (10) *et seq.*), cannot exceed the limiting value,

$$k_0 = 2\lambda^{-1}; \tag{35}$$

moreover, not all the spectra lying within this radius are actually recorded.

In order to estimate the errors introduced into peaks and curvatures by such a finite series let us consider the simpler problem of an isolated atom. The density distribution and the atomic scattering factor are then related by the reciprocal Fourier equations,

$$\left.\begin{aligned} \varrho(\mathbf{r}) &= \int f(\mathbf{k}) \exp(2\pi i\mathbf{k}'\mathbf{r})\,d\mathbf{k}\,, \\ f(\mathbf{k}) &= \int \varrho(\mathbf{r}) \exp(-2\pi i\mathbf{k}'\mathbf{r})\,d\mathbf{r}\,. \end{aligned}\right\} \tag{36}$$

When the distribution has spherical symmetry, the integrations over angular coordinates may be carried out: the transforms become

$$\left.\begin{aligned} \varrho(r) &= 2r^{-1}\int_0^\infty f(k)\sin(2\pi kr)\,k\,dk\,, \\ f(k) &= 2k^{-1}\int_0^\infty \varrho(r)\sin(2\pi kr)\,r\,dr\,. \end{aligned}\right\} \tag{36a}$$

From the former equation we derive formulae for the peak height and curvature:

$$\left.\begin{aligned} P &= 4\pi\int_0^\infty f(k)\,k^2\,dk\,, \\ C &= \frac{16\pi^3}{3}\int_0^\infty f(k)\,k^4\,dk\,. \end{aligned}\right\} \tag{37}$$

The corresponding parameters of the distribution obtained by restricting the range of integration to the sphere, $k < k_0$, in reciprocal space are

$$\left.\begin{aligned} P(k_0) &= 4\pi\int_0^{k_0} f(k)\,k^2\,dk\,, \\ C(k_0) &= \frac{16\pi^3}{3}\int_0^{k_0} f(k)\,k^4\,dk\,. \end{aligned}\right\} \tag{37a}$$

Let us simplify further by using the gaussian approximation (33) to the distribution. Then the second of equations (36) may be integrated to give

$$f(k) = P(2\pi/a')^{\frac{3}{2}}\exp(-2\pi^2k^2/a')\,. \tag{38}$$

Let us define the fractional errors introduced into P and C by the finite reciprocal radius:

$$\mathcal{E}(P) = \{P - P(k_0)\}/P\,,$$
$$\mathcal{E}(C) = \{C - C(k_0)\}/C\,.$$

Then from (33), (37), (37*a*) and (38) we find

$$\left.\begin{aligned} \mathcal{E}(P) &= (2/\sqrt{\pi})\gamma(\tfrac{3}{2};\, 2\pi^2k_0^2/a')\,, \\ \mathcal{E}(C) &= (4/3\sqrt{\pi})\gamma(\tfrac{5}{2};\, 2\pi^2k_0^2/a')\,, \end{aligned}\right\} \tag{39}$$

where γ is the incomplete gamma function,

$$\gamma(n;\, x) = \int_x^\infty e^{-t}t^{n-1}\,dt\,.$$

An application of the recursion formula,

$$\gamma(n+1;\, x) = n\gamma(n;\, x) + x^ne^{-x}\,,$$

to (39) shows that

$$\mathcal{E}(C) = \mathcal{E}(P) + (4/3\sqrt{\pi})(2\pi^2k_0^2/a')^{\frac{3}{2}}\exp(-2\pi^2k_0^2/a')\,,$$

i.e. the error in C is always greater than that in P.

It is of interest to apply equation (39) to the distribution ϱ_g computed in § 6: then $a' = 11{\cdot}24$ Å^{-2}. The wave-length used in the experimental work on naphthalene was $\lambda = 1{\cdot}54$ Å (Abrahams, Robertson & White, 1949*a*), so the appropriate limiting reciprocal radius is not greater than that given by (35), $k_0 = 1{\cdot}30$ Å^{-1}. The corresponding errors are computed to be

$$\mathcal{E}(P) = 0{\cdot}112,\ \mathcal{E}(C) = 0{\cdot}306\,.$$

The parameters of $\bar{\varrho}_g$ are $P = 6{\cdot}955$ e.Å^{-3}, $C = 78{\cdot}16$ e.Å^{-5}; thus the parameters of the modified distribution are

$$P(k_0) = 6{\cdot}18 \text{ e.Å}^{-3},\ C(k_0) = 54{\cdot}2 \text{ e.Å}^{-5}\,,$$

which may be compared with the experimental parameters,

$$P = 6{\cdot}9 \text{ e.Å}^{-3},\ C = 57 \text{ e.Å}^{-5}\,.$$

The theoretical peak has been reduced slightly below the comparable experimental peak, but the agreement between the curvatures is now much more satisfactory. It seems likely that the theoretical distribution having the same $P(k_0)$ as the experimental one would also have approximately the same $C(k_0)$.

8. Discussion

Fig. 1 shows that the effect of vibration on the peak density is considerable: an amplitude of ½ Å reduces it by a factor of more than 100. This is of course due to the sharpness of the peak in the stationary atom. The effect on the bridge densities in bonds is less pronounced, but the calculations of § 6 show that these may be increased by more than 25%. It is therefore impossible to make any useful comparisons between the densities calculated by quantum-

theoretical methods for stationary molecules and the corresponding densities derived from X-ray diffraction measurements, unless the latter are first corrected adequately for thermal motion.

The closeness of $\bar{\varrho}$, as calculated in § 6, to the gaussian curve $\bar{\varrho}_g$ suggests that the distribution at an amplitude such as that which occurs in naphthalene is not very sensitive to the shape of ϱ; for $\bar{\varrho}_g$ depends on ϱ only through the two integrals, ϱ_0 and ϱ_1. Thus many details of the electron distribution in a stationary molecule are likely to be lost in the distribution occurring in a molecular crystal at ordinary temperatures.

The $(\overline{u^2})^{\frac{1}{2}}$—$\bar{\varrho}(0)$ curve may be used to determine the r.m.s. amplitude of a carbon atom having a given observed peak density. It is of interest therefore to examine the assumptions used in the calculations of § 4. These are as follows:

(i) The wave-functions used are those for a free carbon atom. Bonding is neglected except as the source of the potential energy for motion of the nuclei. Since it is mainly the valence $(2s)\,(2p)^3$ electrons which take part in bonding, the inner-shell $(1s)^2$ electrons being practically unaffected, the quantity v (Fig. 2) provides an index of the probable effect of bonding on $\bar{\varrho}(0)$. So long as v is small, the contribution from the valence electrons is relatively unimportant. The range of values of $(\overline{u^2})^{\frac{1}{2}}$ occurring in molecular crystals such as naphthalene and anthracene is 0·4–0·5 Å, corresponding to $\bar{\varrho}(0) = 9{\cdot}5$–$5{\cdot}5$ e.Å^{-3} (data from Abrahams *et al.*, 1949*a*, *b*; Mathieson *et al.*, 1950); in this region $v = 13$–$19\,\%$, so the effect of bonding may be appreciable.

(ii) The atomic wave-functions are those derived by the Hartree method. These are the ones which it is customary to employ in X-ray scattering theory.* Recently McWeeny (1951) has discussed the use of analytical wave-functions in calculating scattering factors for stationary atoms, and in a later paper (1952) he deals with the effects of bonding.

An idea of the importance of the choice of wave-functions may be gained by comparing the value 847 e.Å^{-3}, calculated in § 4 for the stationary peak density, with the value 797 e.Å^{-3}, derived from analytical wave-functions of the form,

$$\psi_{1s}(\mathbf{r}) = g_1 \exp(-\gamma r)\,,$$
$$\psi_{2s}(\mathbf{r}) = g_2(r-\alpha) \exp(-\delta r)\,,$$

where $g_1, g_2, \alpha, \gamma, \delta$ are constants: the difference is about 6%. Now when $(\overline{u^2})^{\frac{1}{2}}$ is large, $\bar{\varrho}$ tends towards the asymptotic form (32), which is independent of the choice of wave-functions. Therefore it is reasonable to suppose that the error in $\bar{\varrho}$ due to any special choice of wave-functions tends to decrease as $(\overline{u^2})^{\frac{1}{2}}$ increases. It is probable then that the error in $\bar{\varrho}(0)$ caused by the assumption (ii) is not worse than, say, 5%.

(iii) Anharmonicity of the vibrations is neglected. The influence of this can be assessed only by a detailed analysis of the spectra of particular crystals. It is probably not important, provided that the amplitudes are not too large.

(iv) The motion is assumed to be isotropic. The effect of anisotropy has been discussed in § 5, where it was found to be small in the example which was examined.

(v) The density at the centre of one atom due to its neighbours has been neglected. This is justified if the bridge densities between the atom and each of its neighbours are small in comparison with the peak density, for the contribution to the peak from a neighbour is presumably much less than half the bridge density.

When all these sources of error have been taken into account, one may conclude that the accuracy of $\bar{\varrho}(0)$ corresponding to a given $(\overline{u^2})^{\frac{1}{2}}$ is probably not worse than 20% in the range covered by Table 2. It follows from equation (26) that the value of $(\overline{u^2})^{\frac{1}{2}}$ corresponding to a given $\bar{\varrho}(0)$ may be calculated with an accuracy not worse than about 10% in the same range.

Finally it may be remarked that the considerations of § 7 indicate that even a comparison between a thermally averaged electron density, such as that which has been computed in this paper, and an experimental density is of little value unless the latter has first been corrected for finite-series errors.

It is a pleasure to record my gratitude to Prof. C. A. Coulson, F.R.S., who suggested this problem to me, for his advice and encouragement throughout the course of the investigation. I am glad to have had an opportunity to discuss the problem with Dr D. W. J. Cruickshank, who first showed me the importance of the finite-series error. My thanks are also due to the University of London for the award of a Postgraduate Studentship and to King's College for a Layton Studentship, during the tenure of which the work was carried out.

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* Actually, the scattering factor for carbon tabulated by James & Brindley (1931), which is frequently used by crystallographers, was derived by interpolation from the Hartree-field scattering factors of various other atoms; the Hartree-field for carbon was not computed until several years later (Torrance, 1934). Moreover the JB factor is designed for the ground state, whereas it seems more reasonable on chemical grounds to consider the valence state, as has been done in this paper.

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APPENDIX II.

VIBRATIONAL MODIFICATIONS OF THE ELECTRON DISTRIBUTION IN MOLECULAR CRYSTALS. II. MEAN SQUARE AMPLITUDES OF THERMAL MOTION.

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ABSTRACT.

The calculation of the mean square amplitude of thermal motion of an atom in a molecular crystal is discussed. It is shown that, with certain simplifying assumptions concerning the form of the force field, there should be a linear relation between the mean square amplitude and the square of the distance of the atom from the molecular centre of mass. The relation is found to hold approximately for naphthalene and anthracene, and its validity and limitations are discussed.

1. INTRODUCTION.

In the first paper of this series (Higgs, 1953; to be referred to henceforth as I) the effective electron density derived from the Laue scattering of X-rays by a crystal was shown to be identical with the thermal average of the density at the temperature of the experiment. An expression (equation I 18) was derived which related this density to the electron distribution in a lattice of stationary atoms and to the mean square amplitudes and mean products of amplitudes of thermal vibration of the atoms in the actual

crystal. The peak density at the centre of a carbon atom was computed as a function of its r.m.s. amplitude of vibration, a Hartree field being assumed for the distribution in the stationary atom and the thermal motion being taken to be isotropic.

In this paper the problem of calculating r.m.s. amplitudes for atoms in molecular crystals is considered, with particular reference to naphthalene and anthracene. In Section 2, two kinds of contribution to the total mean square amplitude $\overline{u^2}$ are distinguished: that of the "rigid-body" vibrations in which each molecule moves as an almost rigid unit, and that arising from the internal normal modes of each molecule, interaction constants between these two types of displacement being neglected. In Section 3 the rigid-body vibrations are classified further into translational and rotational modes, further interaction constants being neglected, and an expression for their contribution to the mean square amplitude is derived from a simple model of the intermolecular force field. The calculation of the contribution from the internal modes of the molecule is discussed in Section 4.

In Section 5 use is made of some unpublished results of Cruickshank (1953) to obtain values of $\overline{u^2}$ in naphthalene and anthracene derived from the published X-ray analyses

(Abrahams, Robertson & White, 1949a,b; Mathieson, Robertson & Sinclair, 1950a,b). It is found that the variation of $\overline{u^2}$ from one atom to another within each molecule is roughly consistent with a thermal motion composed mainly of translation (lattice vibrations) and isotropic rotation (librations). The validity and limitations of this interpretation are discussed in Section 6.

The Appendix contains the derivation of some formulae used in the body of the paper.

2. INTERNAL AND RIGID-BODY CONTRIBUTIONS TO $\overline{u^2}$.

In any discussion of the vibrations of a molecular crystal it is useful to distinguish between coordinates describing the internal distortion of the molecules and those describing their relative motion. If we consider a general small displacement of the n atoms in a single molecule from their equilibrium configuration, we may completely specify the internal distortion by the $3n - 6$ components ($3n - 5$ for a linear molecule) of a column vector $\underline{y}$ and the movement of the molecule as a whole by the 6 components (5 for a linear molecule) of a column vector $\underline{\eta}$. The former consist of extensions of bonds, distortions of

bond-angles, torsions of bonds, etc; the latter of translations and rotations of the whole molecule. An alternative description is provided by another column vector $\underline{x}$, whose $3n$ components specify the atomic displacements relative to a triad of Cartesian axes fixed in space: we adopt the convention that the components x_j ($j = 3i-2, 3i-1, 3i$) refer to the ith atom and denote these briefly by the 3-vector $\underline{u}_i$.

For small displacements the alternative systems are related linearly by a coordinate transformation which may be written as

$$\underline{x} = \underline{a}\underline{y} + \underline{\alpha}\underline{\eta}, \tag{1}$$

or as the inverse equations,

$$\underline{y} = \underline{b}\underline{x}, \tag{2}$$

$$\underline{\eta} = \underline{\beta}\underline{x}. \tag{3}$$

As is shown in the Appendix, the rectangular matrices $\underline{\alpha}$ and $\underline{b}$ may be written down immediately in terms of the geometry of the molecule. If the transformation is completed by the definitions,

$$\underline{a} = \underline{M^{-1} b' G^{-1}}, \tag{4}$$

$$\underline{\beta} = \underline{\Phi^{-1} \alpha' M}, \tag{5}$$

where $\underline{M}$ is the diagonal matrix of atomic masses ($M_{jj} = m_i$, for $j = 3i-2, 3i-1, 3i$) and

$$\underline{G} = \underline{b\, M^{-1}\, b'}, \tag{6}$$

$$\underline{\Phi} = \underline{\alpha'\, M\, \alpha}, \tag{7}$$

then the kinetic energy splits up into two independent parts, the one arising from internal distortion, the other from motion of the molecule as a rigid body:

$$T = \tfrac{1}{2}\,\dot{\underline{y}}'\,\underline{G^{-1}}\,\dot{\underline{y}} + \tfrac{1}{2}\,\dot{\underline{\eta}}'\,\underline{\Xi}\,\dot{\underline{\eta}}. \qquad (8)$$

This equation was first derived by Wilson (1939) for the special case, $\underline{\eta} = \underline{0}$.

The potential energy of a free molecule depends only on its internal distortion and may be written in the first (harmonic) approximation as

$$V = \tfrac{1}{2}\,\underline{y}'\,\underline{F_0}\,\underline{y}\,, \qquad (9)$$

where $\underline{F_0}$ is a matrix of force constants and interaction constants. It is obvious from inspection of equations (8) and (9) that the normal coordinates for molecular vibrations fall into two distinct sets: the first set, $\underline{q_1}$, consists of linear combinations of $\underline{y}$ and corresponds to frequencies ν_0 which are solutions of the secular equation for internal vibrations,

$$|\underline{G\,F_0} - 4\,\pi^2\,\nu_0^2\,\underline{I}| = 0; \qquad (10)$$

the second, $\underline{q_2}$, is formed from $\underline{\eta}$ and describes free rigid-body motion ($\nu = 0$).

When the molecule is situated in a crystal equation (9) is no longer valid: the potential energy is, in the harmonic approximation, of the more general form,

$$V = \tfrac{1}{2} \sum_{\rho,\sigma=1}^{N} \{\underline{y'_\rho\,F_{\rho\sigma}\,y_\sigma} + \underline{\eta'_\rho\,K_{\rho\sigma}\,\eta_\sigma} + 2\,\underline{y'_\rho\,k_{\rho\sigma}\,\eta_\sigma}\}, \qquad (11)$$

in which the vectors $\underline{y}_\rho$ and $\underline{\eta}_\rho$ refer to the ρ th molecule of the N which constitute the crystal. The intermolecular forces are here represented by the matrices $\underline{K}_{\rho\sigma}$, $\underline{k}_{\rho\sigma}$ (all ρ,σ), $\underline{F}_{\rho\sigma}$ ($\rho \neq \sigma$) and $(\underline{F}_{\rho\rho} - \underline{F}_o)$. In general, owing to the presence of the last term in (11), it is no longer possible rigorously to separate the normal modes into internal and rigid-body vibrations of the molecules. However, there is ample spectroscopic evidence that most of the vibration frequencies of many organic molecules do not depend to any large extent on the physical state of the substance. That is, as one would expect, the intermolecular forces are much weaker than the intramolecular forces: in (11) $\underline{F}_{\rho\rho} \doteq \underline{F}_o$, $\underline{F}_{\rho\sigma} \doteq \underline{0}$ ($\rho \neq \sigma$) and the elements of $\underline{k}$ are small compared with those of $\underline{F}_o$. Therefore it seems reasonable to neglect $\underline{k}$ and use the simplified potential,

$$V = \tfrac{1}{2} \sum_{\rho=1}^{N} \underline{y'_\rho \; F_o \; y_\rho} + \tfrac{1}{2} \sum_{\rho,\sigma=1}^{N} \underline{\eta'_\rho K_{\rho\sigma} \eta_\sigma}. \qquad (12)$$

The separation of the normal coordinates into $\underline{q_1}$ and $\underline{q_2}$ is now valid once more.

In these circumstances it is possible to effect a corresponding decomposition of $\overline{u_i^2}$, the mean square amplitude of thermal motion of the ith atom in any molecule: for $\underline{u_i}$ is related to $\underline{q_1}$ and $\underline{q_2}$ by a linear transformation,

$$\underline{u_i} = \underline{c_{i1} \; q_1} + \underline{c_{i2} \; q_2},$$

from which it follows that

$$\overline{u_i^2} = \text{trace}\left\{\underline{c_{i1}\,\overline{q_1 q_1'}\,c_{i1}'} + \underline{c_{i2}\,\overline{q_2 q_2'}\,c_{i2}'}\right\}. \qquad (13)$$

($\underline{q_1}$ and $\underline{q_2}$ being different sets of normal coordinates, $\underline{\overline{q_1 q_2'}} = \underline{0}$.) The two terms of (13) may be interpreted as the contributions from internal and rigid-body modes respectively:

$$\overline{u_i^2} = \left(\overline{u_i^2}\right)_{\text{int}} + \left(\overline{u_i^2}\right)_{\text{r-b}}. \qquad (14)$$

The intermolecular forces being comparatively weak, the second term of (14) is by far the larger of the two, and to the first may be assigned the value appropriate to a free molecule.

3. AN APPROXIMATE EXPRESSION FOR $\left(\overline{u_i^2}\right)_{\text{r-b}}$.

It is shown in the Appendix that the rigid-body term in the kinetic energy (8) may be written (as in A14) as the sum of independent terms arising from translation of the centre of mass (η_t) and rotation about that centre (η_r). Let us assume a model for the intermolecular potential such that there is no interaction between translation and rotation, i.e.

$$V_{\text{r-b}} = \tfrac{1}{2}\sum_{\rho,\sigma}\left\{\underline{\eta'_{t\rho}\,K_{t\rho\sigma}\,\eta_{t\sigma}} + \underline{\eta'_{r\rho}\,K_{r\rho\sigma}\,\eta_{r\sigma}}\right\}. \qquad (15)$$

There being now no cross-terms in either the kinetic or the potential energy, $(\overline{u_i^2})_{r-b}$ is the sum of two terms, one arising from translation (the lattice or "acoustic" modes), the other from restricted rotation (libration):

$$(\overline{u_i^2})_{r-b} = (\overline{u_i^2})_t + (\overline{u_i^2})_r. \qquad (16)$$

Let us consider the dependence of these terms on the position of atom i in the molecule. Whatever the form of the first term of (15) may be, it is obvious that $(\overline{u_i^2})_t$, arising as it does from translation, is the same for all atoms:

$$(\overline{u_i^2})_t = A, \qquad (17)$$

where A is some function of the temperature.

On the other hand $(\overline{u_i^2})_r$ varies from atom to atom in a way which depends on the form of the second term of (15). In view of the present scarcity of evidence concerning this force field for libration it seems to be necessary to adopt some simple model. Let us assume that each molecule rotates in a time-independent external field, which may be regarded as an average of that due to interactions with its neighbours, and that this field does not depend on the direction of the axis of rotation. Then the second term of (15) contains no cross-terms between the coordinates of different molecules, and the potential for rotation of a single molecule may be

written as

$$V_r = \tfrac{1}{2} K_r \underline{\eta_r' \eta_r}\ , \qquad (18)$$

where K_r is a force constant for libration.

In order to calculate $(\overline{u^2_i})_r$ we require an expression for the thermal average $\overline{\underline{\eta_r \eta_r'}}$. The general expression for such a matrix is that of I (8): it leads to the formula,

$$\overline{\underline{\eta_r \eta_r'}} = \tfrac{1}{2}\hbar (K_r \underline{\Phi}_r)^{-\frac{1}{2}} \coth(\hbar K_r^{\frac{1}{2}} \underline{\Phi}_r^{-\frac{1}{2}}/2kT), \qquad (19)$$

in which T is the thermodynamic temperature and $\hbar$ and k have their usual significance. Now the spectroscopic evidence indicates that the libration frequencies of molecular crystals are quite low, usually in the region of 100 cm^{-1} (see for example Rousset, 1948). Since these frequencies are the solutions of the secular equation

$$|\underline{\Phi}_r^{-1} K_r - 4\pi^2 c^2 \tilde{\nu}^2 \underline{I}| = 0\ ,$$

the argument of the function in (19) is essentially $\hbar c\tilde{\nu}/2kT$. At ordinary temperatures ($T \sim 290^\circ K$) and with $\tilde{\nu} \sim 100$ cm^{-1} this quantity is small enough for the approximation, $\coth x \doteq x^{-1}$, to be a good one: (19) becomes

$$\overline{\underline{\eta_r \eta_r'}} \doteq kT\, \underline{I} / K_r. \qquad (20)$$

(This approximation is essentially that of classical mechanics, $\hbar = 0$.)

From equations (20) and (A1) it follows that

$$(\overline{u^2_i})_r = 2k\,T\,R_i^2/K_r, \tag{21}$$

where R_i is the distance of atom i from the molecular centre of mass.

Combining (16), (17) and (21) we obtain for the total contribution from rigid-body modes

$$(\overline{u^2_i})_{r\text{-}b} = A + B\,R_i^2, \tag{22}$$

in which A and B are temperature-dependent.

4. THE CALCULATION OF $(\overline{u^2_i})_{int}$

It is evident from equations (1), (8), (9) and I(8) that the formula from which $(\overline{u^2_i})_{int}$ must be calculated is

$$(\overline{u^2_i})_{int} = \sum_{j=3i-2}^{3i} \underline{a}_j\,\overline{\underline{y}\underline{y}^T}\,\underline{a}'_j \tag{23}$$

in which

$$\overline{\underline{y}\underline{y}^T} = \tfrac{1}{2}\hbar\,(\underline{G}\underline{F}_o)^{-\frac{1}{2}} \coth\left\{\hbar\,(\underline{G}\underline{F}_o)^{\frac{1}{2}}/2kT\right\}\underline{G}, \tag{24}$$

where $\underline{G}$ is defined by equation (6), and $\underline{a}_j$ is the jth row of $\underline{a}$. Using (4) and (24), we transform (23) into the form

$$(\overline{u^2_i})_{int} = \tfrac{1}{2}\hbar\,m_i^{-2} \sum_{j=3i-2}^{3i} \underline{b}_j\,\underline{G}^{-1}(\underline{G}\underline{F}_o)^{-\frac{1}{2}} \coth\left\{\hbar\,(\underline{G}\underline{F}_o)^{\frac{1}{2}}/2kT\right\}\underline{b}_j. \tag{25}$$

where $\underline{b}_j$ is the j th column of $\underline{b}$. If the vibration frequencies ν_o, found by solving equation (10), are low ($h\nu_o/kT \ll 1$), we may use the approximation $\coth z \doteq z^{-1}$ ($z \ll 1$) to simplify (25) as follows:

$$(\overline{u^2_i})_{int} \doteq kTm_i^{-2} \sum_{j=3i-2}^{3i} \underline{b'_j (GF_oG)^{-1} b_j}. \qquad (26)$$

Conversely, if the frequencies are high ($h\nu_o/kT \gg 1$), the asymptotic relation $\coth z \sim 1$ ($z \to \infty$) leads to the approximate formula

$$(\overline{u^2_i})_{int} \doteq \tfrac{1}{2} h m_i^{-2} \sum_{j=3i-2}^{3i} \underline{b'_j G^{-1} (GF_o)^{-\frac{1}{2}} b_j}. \qquad (27)$$

Equations (26) and (27) are respectively the classical and zero-point limits of (25). These results enable us to calculate $(\overline{u^2_i})_{int}$ from the geometry of the molecule, as expressed by the transformation matrix $\underline{b}$, and any hypothetical force field $\underline{F}_o$.

The choice of $\underline{F}_o$ depends upon two considerations: on the one hand we have ideas concerning the general form of the field based on quantum theoretical treatments of the electronic structure; on the other hand we want the solutions ν_o of equation (10) to agree as closely as possible with the

fundamental vibration frequencies determined spectroscopically. In practice, a compromise is usually attempted, for most of the a priori quantum mechanical calculations carried out so far do not lead to very good quantitative agreement with the observed spectra.

In the main, force fields are constructed by semi-empirical procedures having as their point of departure the "simple valence force field" introduced by Bjerrum (1914): $\underline{F}_0$ is taken to consist mainly of force constants which may be transferred between similar structural units of related molecules, and small off-diagonal interaction constants are postulated to account for details of the spectra. These extra constants have been interpreted theoretically by Coulson, Duchesne & Manneback (1948) in terms of resonance effects, changes of hybridization and interactions between non-bonded atoms. Such procedures are quite successful in dealing with molecules built from simple atomic groupings linked by chains of single bonds, but less so in coping with conjugated systems, where the form of the field is determined largely by the mobile electrons and the resulting interaction constants are large. It is in describing fields of the latter type that a theoretical approach is most helpful: for example, Coulson & Longuet-Higgins (1948) have shown how these fields may be obtained by the simple molecular

orbital technique in terms of such quantities as the mobile orders and the self and mutual polarizabilities of the bonds.

A calculation of the type described in this section has been carried out on the carbon skeleton of naphthalene in order to find the relative magnitudes of $(\overline{u^2_i})_{int}$ for the various carbon atoms: the details of this calculation were described in the author's M.Sc. thesis (Higgs, 1952, Chapter 4). The assumed force field was that given by Coulson & Longuet-Higgins (loc. cit.) with the addition of force constants for bending of the skeleton; the same field for in-plane vibrations was used by Jacobs (1951) in her calculation of the A_g frequencies. The formula employed was (26), although at 20°C, the temperature at which the X-ray measurements of Abrahams, Robertson & White (1949a) were carried out, the ratios $h\nu_0/kT$ could hardly be called small (see Higgs, loc. cit.); nevertheless, it was thought that the simple classical approximation would give some indication of the variation of $(\overline{u^2_i})_{int}$ over the molecule. The results of the calculation are given in Table 1.

5. EXPERIMENTAL VALUES OF $\overline{u^2_i}$: NAPHTHALENE AND ANTHRACENE.

In order to test the validity of equation (22) let us consider the values of $\overline{u^2_i}$ in naphthalene and anthracene at

20°C, for which the detailed results of X-ray analyses are available (Abrahams, Robertson & White, 1949a,b; Mathieson, Robertson & Sinclair, 1950a,b). Ahmed and Cruickshank (1952) have refined the crystal and molecular structures by a method which minimizes the mean difference between the observed structure factors and those calculated from a model with atoms arranged in roughly the expected configuration. In their earlier calculations they assigned to the various carbon atoms the same isotropic vibration amplitude, but more recently (Cruickshank, 1953) they have used a more flexible method which allows for different isotropic thermal motions. Values of $\overline{u_i^2}$ derived from Cruickshank's B values are given in Tables 1 and 2. (The B value for an atom is a parameter in its temperature factor, isotropic thermal motion being assumed. In the notation of I it is defined by the relation

$$g_i = f_i \exp(-B_i \sin^2\theta/\lambda^2) \qquad (28)$$

connecting the scattering factor for a vibrating atom with that for a stationary one. It follows from equations (28), I (9) and (11a) that

$$\overline{u_i^2} = 3B_i/8\pi^2.)$$

We may now find $(\overline{u_i^2})_{r-b}$, for naphthalene at least, by subtracting from each $\overline{u_i^2}$ the appropriate value of $(\overline{u^2}_i)_{int}$ calculated in Section 4: these quantities are also tabulated

in Table 1. The corresponding values of R_i^2 are calculated on the assumption that the carbon atoms lie at the vertices of coplanar regular hexagons (Figure 1). When $(u^2_i)_{r-b}$ is plotted against R_i^2/l^2, where l is the CC bond length, the three points (A, B, C) lie reasonably close to a straight line (Figure 3, middle graph).

Since no calculations of $(\overline{u_i^2})_{int}$ have been made for anthracene, we cannot plot values of $(\overline{u^2_i})_{r-b}$ for this molecule. However, as is shown in Figure 3 (topmost graph), the $(u_i^2)_{int}$ values for naphthalene vary so little - they are in any case only about 4% of the total $\overline{u_i^2}$ - that the graph of $\overline{u_i^2}$ itself against R_i^2/l^2 is nearly linear. So we may expect that if, as is very likely, the anthracene $(\overline{u^2_i})_{int}$ values vary only slightly over the molecule, the graph of $\overline{u_i^2}$ against R_i^2/l^2 will again be nearly linear: this is indeed what happens (Figure 3, bottom graph; the data are taken from Table 2, and the labelling of the atoms is illustrated in Figure 2).

6. DISCUSSION.

It appears from the foregoing considerations that, for naphthalene and anthracene at least, the formula (22) provides quite a good approximate description of the thermal

motion: the implication is that most of the variation in the carbon peak densities noticed by Robertson et al. may be accounted for in terms of Fourier series termination errors (allowed for by the methods of Ahmed and Cruickshank) and thermal libration. However it must be stressed that this conclusion is only provisional. The data supplied by Cruickshank are the results of preliminary work and may be modified slightly by further calculations. Besides, these data are scarcely sufficient to establish the linearity of the $\overline{u^2}$ vs. R^2 relation.

Finally, there are a few comments to be made on the deviations of the experimental points from strict linearity, if in fact these are significant: in particular we may note that atoms C and D in anthracene, having the same value of R_1, do not have equal $\overline{u_1^2}$ values. The calculated $(\overline{u_1^2})_{int}$ values are so small compared with the total $\overline{u_1^2}$ that we may probably discount internal molecular vibrations as a cause of these deviations. A much more likely explanation is that they are due to anisotropy of the librations, for to assign an isotropic force field (equation 18) to a molecule in such an anisotropic environment as a polyacene crystal is really a drastic oversimplification; no doubt further work on the anisotropy of the atomic motions, as revealed by the X-ray data, will throw some light on this matter.

Moreover, to return to the problem which provided the starting point for this investigation, there must be some error in the $\overline{u^2}_i$ values deduced from the X-ray data due to the use of scattering factors for isolated atoms; any redistribution of electronic charge occurring during bonding will give rise to departures from linearity in the graph of apparent $\overline{u^2}_i$ vs. R_i^2. There is an obvious need for further investigations to distinguish decisively between the effects of thermal motion and those of charge transfer.

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APPENDIX.

Given the definition of the quantities $\underline{y}$, we may write the matrix $\underline{b}$ of equation (2) in terms of the geometry of the molecule. General formulae for several commonly used types of internal coordinate have been given by Wilson (1939, 1941): for example, if a particular coordinate y is the extension of the bond connecting atoms i and j, then y is related to $\underline{x}$ by the formula (in 3-vector notation),

$$y = \frac{(\underline{U}_i - \underline{U}_j).(\underline{u}_i - \underline{u}_j)}{|\underline{U}_i - \underline{U}_j|} ,$$

where $\underline{U}_i$ is the 3-vector defining the equilibrium position of atom i relative to the origin of the cartesian coordinates.

Similarly, in (1) the matrix $\underline{\alpha}$ may be written in terms of the molecular geometry : if η_1, η_2, η_3 (3-vector $\underline{\eta}_t$) are the Cartesian components of the displacement of a certain point in the molecule during a small rigid-body motion ($\underline{y} = \underline{0}$), and η_4, η_5, η_6 (3-vector $\underline{\eta}_r$) are the components relative to the Cartesian axes of the rotation of the molecule during such a motion, then during the motion the displacement of atom i is (in 3-vector notation)

$$\underline{u}_i = \underline{\eta}_t + \underline{\eta}_r \wedge \underline{R}_i \quad , \qquad (A1)$$

in which

$$\underline{R}_i = \underline{U}_i - \underline{U}_0 , \qquad (A2)$$

where $\underline{U}_0$ is the equilibrium position of the reference point relative to the Cartesian origin. Equation (A1) constitutes rows $3i-2$, $3i-1$, $3i$ of (1) with $\underline{y} = \underline{0}$, thus defining $\underline{\alpha}$.

We now have $\underline{y}$ defined generally and $\underline{\eta}$ defined only for rigid-body motion; to define the coordinates completely we need to generalize the definition of $\underline{\eta}$, that is, to find the matrix $\underline{\beta}$ of (3): the matrix $\underline{a}$ of the inverse equation (1) will then be defined uniquely. So far the only known relations between the unknown matrices, $\underline{a}, \underline{\beta}$, and $\underline{\alpha}, \underline{b}$ are those expressing the reciprocal nature of (1) and (2), (3):

$$\underline{a}\,\underline{b} + \underline{\alpha}\,\underline{\beta} = \underline{I}; \qquad (A3)$$

$$\left.\begin{aligned} \underline{b}\,\underline{a} &= \underline{I}_1, \underline{b}\,\underline{\alpha} = \underline{0}, \\ \underline{\beta}\,\underline{a} &= \underline{0}, \underline{\beta}\,\underline{\alpha} = \underline{I}_2, \end{aligned}\right\} \qquad (A4)$$

where $\underline{I}_1$, $\underline{I}_2$ are the unit matrices of orders $(3n-6)$, 6 respectively. These equations are not sufficient to define $\underline{a}, \underline{\beta}$ uniquely.

To make the problem soluble uniquely we add the requirement that the kinetic energy shall be expressible as the sum of independent contributions from the velocities $\dot{\underline{y}}$ and $\dot{\underline{\eta}}$. In Cartesians the kinetic energy is

$$T = \tfrac{1}{2}\, \dot{\underline{x}}'\, \underline{M}\, \dot{\underline{x}} ;$$

using (1) we express it in terms of $\underline{\dot{y}}$ and $\underline{\dot{\eta}}$ as

$$T = \tfrac{1}{2}\,\underline{\dot{y}}'\,(\underline{a}'\underline{M}\underline{a})\,\underline{\dot{y}} + \tfrac{1}{2}\,\underline{\dot{\eta}}'\,(\underline{\alpha}'\underline{M}\underline{\alpha})\,\underline{\dot{\eta}} + \underline{\dot{y}}'\,(\underline{a}'\underline{M}\underline{\alpha})\,\underline{\dot{\eta}}\ . \qquad (A5)$$

We require the cross-term in (A5) to be identically zero:

$$\underline{a}'\,\underline{M}\,\underline{\alpha} = \underline{0}\ . \qquad (A6)$$

Equation (A6) may be regarded as a set of $3n-6$ relations between the rows of $\underline{\alpha}$; so also may the second equation of (A4). Since the 6 coordinates $\underline{\eta}$ are linearly independent, the $3n \times 6$ matrix $\underline{\alpha}$ is of rank 6, so there are precisely $3n-6$ linearly independent relations between its rows. Thus the sets of (A4) and (A6) must be equivalent ways of writing the same relations, that is, $\underline{a}'\underline{M}$ must be expressible in terms of $\underline{b}$:

$$\underline{a}'\underline{M} = \underline{A}\underline{b}, \qquad (A7)$$

where $\underline{A}$ is a regular $(3n-6)^2$ matrix. All that remains now is to determine $\underline{A}$: this is done by using (A7) and the first equation of (A4):

$$\underline{b}\,\underline{M}^{-1}\,\underline{b}'\,\underline{A}' = \underline{I}_1,$$

whence

$$\underline{A} = \underline{G}^{-1}, \qquad (A8)$$

where $\underline{G}$, defined in (6), is Wilson's inverse kinetic energy matrix. Equations (4) and (8) now follow from (A5), (A7) and (A8); equation (5) is obtained by premultiplying (A3) by $\underline{\alpha}'\underline{M}$ and using (A6).

From equation (A1) we may derive the explicit form of

the "total inertia matrix" $\underline{\Phi}$, defined in (7). If we denote the jth row of $\underline{\alpha}$ by $\underline{\alpha}_j$, then by comparing (1) and (A1) we find

$$\begin{pmatrix} \alpha_{3i-2} \\ \alpha_{3i-1} \\ \alpha_{3i} \end{pmatrix} = \begin{pmatrix} 1, 0, 0, 0, Z_i, -Y_i \\ 0, 1, 0, -Z_i, 0, X_i \\ 0, 0, 1, Y_i, -X_i, 0 \end{pmatrix},$$

where X_i, Y_i, Z_i are the Cartesian components of $\underline{R}_i$. Equation (7) now becomes

$$\underline{\Phi} = \sum_{i=1}^{n} m_i \begin{pmatrix} 1, 0, 0, 0, Z_i, -Y_i \\ 0, 1, 0, -Z_i, 0, X_i \\ 0, 0, 1, Y_i, -X_i, 0 \\ 0, -Z_i, Y_i, Y_i^2+Z_i^2, -X_iY_i, -X_iZ_i \\ Z_i, 0, -X_i, -Y_iX_i, Z_i^2+X_i^2, -Y_iZ_i \\ -Y_i, X_i, 0, -Z_iX_i, -Z_iY_i, X_i^2+Y_i^2 \end{pmatrix}. \quad \text{(A9)}$$

It is obvious on inspecting (A9) that $\underline{\Phi}$ may be simplified by choosing the centre of mass as the reference point for defining $\underline{\eta}_t$, that is,

$$\underline{U}_o = m^{-1} \sum_{i=1}^{n} m_i \underline{U}_i, \qquad \text{(A10)}$$

where

$$m = \sum_{i=1}^{n} m_i. \qquad \text{(A11)}$$

For (A10) may be written as

$$\sum_{i=1}^{n} m_i \underline{R}_i = \underline{0},$$

so (A9) becomes

$$\underline{\Phi} = \begin{pmatrix} m\underline{I} & , & \underline{0} \\ \underline{0} & , & \underline{\Phi}_r \end{pmatrix}, \qquad \text{(A12)}$$

in which $\underline{\Phi}_r$ is the tensor of moments and products of inertia relative to the centre of mass:

$$\underline{\Phi}_r = \sum_{i=1}^{n} m_i \begin{pmatrix} Y_i^2+Z_i^2 & , & -X_i Y_i & , & -X_i Z_i \\ -Y_i X_i & , & Z_i^2+X_i^2 & , & -Y_i Z_i \\ -Z_i X_i & , & -Z_i Y_i & , & X_i^2+Y_i^2 \end{pmatrix}. \qquad \text{(A13)}$$

The rigid-body term in the kinetic energy (8) now splits up again into two terms,

$$T_{r\text{-}b} = \tfrac{1}{2} m \dot{\underline{\eta}}_t' \dot{\underline{\eta}}_t + \tfrac{1}{2} \dot{\underline{\eta}}_r' \underline{\Phi}_r \dot{\underline{\eta}}_r . \qquad \text{(A14)}$$

The definition (3) of $\underline{\eta}$ may be written explicitly in 3-vector notation ($\underline{\Phi}_r$ being regarded as a dyadic) as

$$\underline{\eta}_t = m^{-1} \sum_{i=1}^{n} m_i \underline{u}_i , \qquad \text{(A15)}$$

$$\underline{\eta}_r = \underline{\Phi}_r^{-1} \left\{ \sum_{i=1}^{n} m_i \underline{R}_i \wedge \underline{u}_i \right\} : \qquad \text{(A16)}$$

these vectors are now the displacement of the centre of mass and the mean rotation about that centre respectively, and $\underline{R}_i$ is the vector from that point to atom i in the equilibrium configuration.

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TABLE 1.

Mean square amplitudes in naphthalene.

Atom	$(\overline{u^2_i})_{int}$ ($\AA^2$)	$\overline{u^2_i}$ ($\AA^2$)	$(\overline{u^2_i})_{r-b}$ ($\AA^2$)	R_i^2/l^2
A	0.005	0.180	0.175	3.25
B	0.006	0.159	0.153	1.75
C	0.004	0.129	0.125	0.25

TABLE 2.

Mean square amplitudes in anthracene.

Atom	$\overline{u^2_i}$ ($\AA^2$)	R_i^2/l^2
A	0.152	7
B	0.131	4
C	0.096	1
D	0.108	1

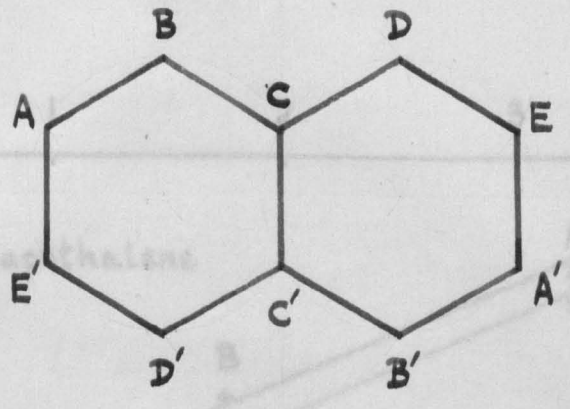

Figure 1. Naphthalene.

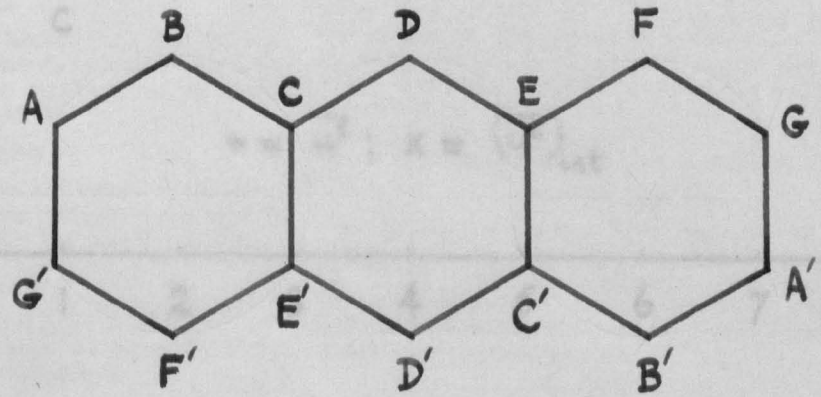

Figure 2. Anthracene.

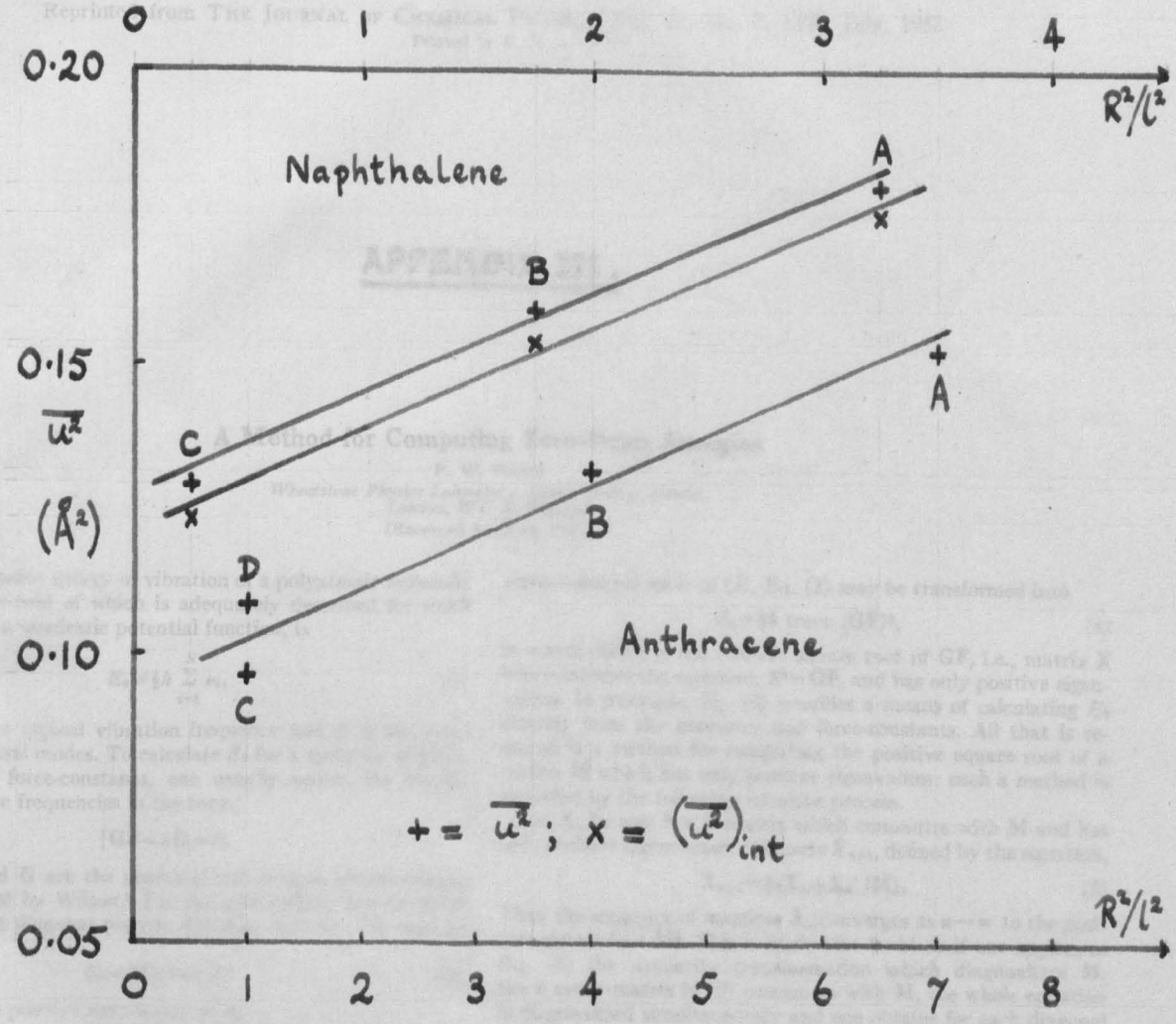

Figure 3. Variation of $\overline{u^2}$ with R^2.

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APPENDIX III.

A Method for Computing Zero-Point Energies

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THE zero-point energy of vibration of a polyatomic molecule, the force-field of which is adequately described for small amplitudes by a quadratic potential function, is

$$E_0=\tfrac{1}{2}h\sum_{i=1}^{N}\nu_i, \tag{1}$$

in which ν_i is a typical vibration frequency and N is the total number of normal modes. To calculate E_0 for a molecule of given geometry and force-constants, one usually solves the secular equation for the frequencies in the form,

$$|\mathbf{GF}-\lambda\mathbf{I}|=0,$$

in which $\mathbf{F}$ and $\mathbf{G}$ are the potential and inverse kinetic-energy matrices defined by Wilson,[1] $\mathbf{I}$ is the unit matrix, and $\lambda=4\pi^2\nu^2$. In terms of the diagonal matrix, $\mathbf{\Lambda}=\text{diag}\,(\lambda_i)$, Eq. (1) may be rewritten as

$$E_0=\tfrac{1}{2}h\,\text{trace}\,\mathbf{\Lambda}^{\frac{1}{2}}, \tag{2}$$

where $\mathbf{\Lambda}^{\frac{1}{2}}$ is the positive square root of $\mathbf{\Lambda}$.

Now the equation which determines the amplitudes of the internal coordinates $\mathbf{y}$ in the ith normal mode is

$$\mathbf{GF}\mathbf{y}_i=\lambda_i\mathbf{y}_i;$$

the set of these equations may be written in terms of the matrix $\mathbf{Y}$ which has $\mathbf{y}_i$ for its ith column as

$$\mathbf{\Lambda}=\mathbf{Y}^{-1}\mathbf{GFY}. \tag{3}$$

By using the invariance of the trace of a matrix under a similarity transformation such as (3), Eq. (2) may be transformed into

$$E_0=\tfrac{1}{2}h\,\text{trace}\,(\mathbf{GF})^{\frac{1}{2}}, \tag{4}$$

in which $(\mathbf{GF})^{\frac{1}{2}}$ is the positive square root of $\mathbf{GF}$, i.e., matrix $\mathbf{X}$ which satisfies the equation, $\mathbf{X}^2=\mathbf{GF}$, and has only positive eigenvalues. In principle, Eq. (4) provides a means of calculating E_0 directly from the geometry and force-constants. All that is required is a method for computing the positive square root of a matrix $\mathbf{M}$ which has only positive eigenvalues: such a method is provided by the following iterative process.

Let $\mathbf{X}_n$ be any $N\times N$ matrix which commutes with $\mathbf{M}$ and has only positive eigenvalues. Compute $\mathbf{X}_{n+1}$, defined by the equation,

$$\mathbf{X}_{n+1}=\tfrac{1}{2}(\mathbf{X}_n+\mathbf{X}_n^{-1}\mathbf{M}). \tag{5}$$

Then the sequence of matrices $\mathbf{X}_n$ converges as $n\to\infty$ to the positive square root $\mathbf{M}^{\frac{1}{2}}$. This is easily seen to be so if one applies to Eq. (5) the similarity transformation which diagonalizes $\mathbf{M}$. Since every matrix in (5) commutes with $\mathbf{M}$, the whole equation is diagonalized simultaneously and one obtains for each diagonal element the well-known sequence,

$$x_{n+1}=\tfrac{1}{2}(x_n+x_n^{-1}m),$$

which converges rapidly to $m^{\frac{1}{2}}$ when x_n is positive. A suitable starting value for the iteration is $\mathbf{X}_0=x_0\mathbf{I}$, where x_0 is any positive number.

I would like to thank Professor H. C. Longuet-Higgins for drawing my attention to this problem.

[1] E. B. Wilson, Jr., J. Chem. Phys. **7**, 1047 (1939); **9**, 76 (1941).